A SMALLER
CHEMICAL ANALYSIS

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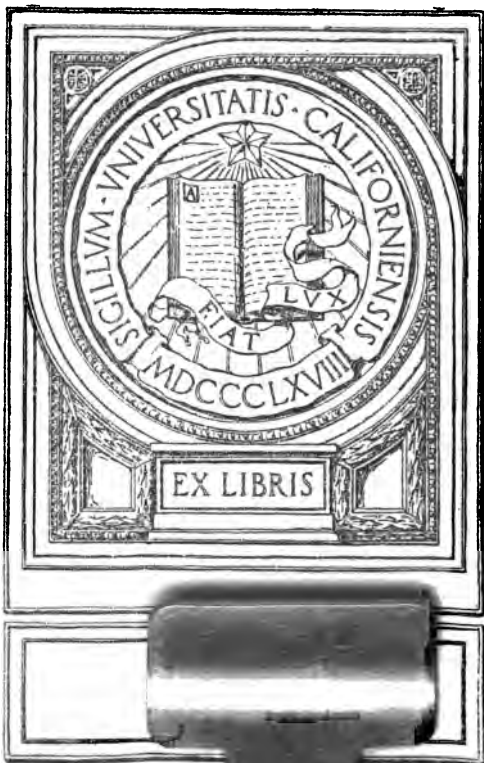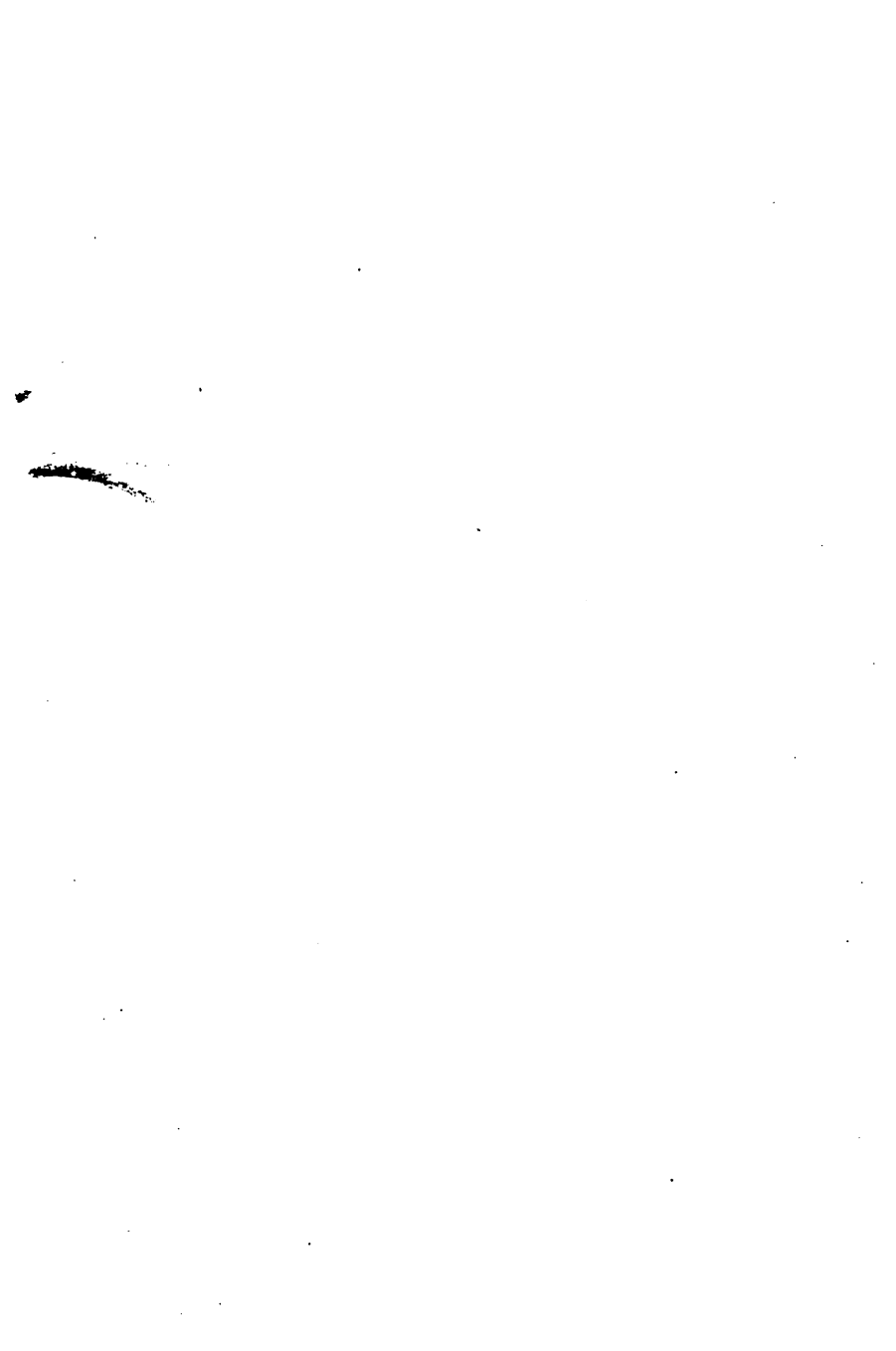
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CHEMICAL ANALYSIS

BY

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IN MEMORIAM

PREFACE

THIS little book is practically an abridged edition of the qualitative section of my *Manual of Chemical Analysis*, and is designed for the use of students who are taking a less advanced stage than those for whom the larger book is intended.

I have included in this book, however, a chapter on such simple volumetric processes as it is customary to introduce into moderately elementary courses of Practical Chemistry.

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CHAPTER I

PRELIMINARY EXERCISES

THE first step that the student must take in approaching the subject of analytical chemistry, is that of making himself *practically* familiar with certain simple operations or manipulations which he will constantly be required to carry out in the course of his work, and upon the dexterous and cleanly performance of which much of his success will depend. If he has not had previous experience in practical chemistry, therefore, he should carefully go through the following exercises.

1. **Filtration.**—The method by which a liquid is separated from any solid substance with which it is mechanically mixed, is most usually that of filtering the mixture through porous paper, known as *filter-paper.*

EXERCISE 1.—Fold a circular filter-paper into half, and then at right angles into half again. Open this into a cone having one thickness of paper on one side and three on the other. This cone is then placed in a glass funnel of such a size that the glass will project slightly *above* the paper. The paper is then moistened with distilled water, which should not be poured out of the funnel again, but allowed to run through. After being cautiously pressed into the glass funnel, the paper should fit close to the glass all round, leaving no air-spaces. If this is not the case, either another funnel of the right angle (60 degrees) should be selected, or another filter-paper folded so that the cone shall be of the same angle as the funnel. The funnel is supported by a metal or wooden stand.

Now place some diluted hydrochloric acid in a small beaker,

and stir into it, by means of a glass rod, a quantity of finely powdered charcoal. When thoroughly mixed, pour upon the filter. When *slowly* pouring from a wide vessel like a beaker, there is risk of some of the liquid being spilt by running down the outside of the vessel, as shown in Fig 1. If it be poured *quickly*, it is likely to splash over the funnel. To prevent both of these accidents, the liquid should be poured down against a glass rod held

Fig. 1.   Fig. 2.

lightly against the edge of the beaker, and in such a position that the liquid does not strike at once against the apex of the paper cone (Fig. 2).

The *filtrate* (*i.e.* the liquid which passes through the filter) may be received in another beaker, which should be placed close against the stem of the funnel, so that the liquid shall run down against the glass. In this way splashing is prevented. The filtrate should be perfectly clear, the whole of the solid being retained on the filter. When all the liquid has passed through, the charcoal and the filter-paper are both still soaked with the hydrochloric acid. In order to remove this, and so to make the separation of the solid from the liquid complete, the

filter and its contents must be washed with distilled water.[1] This is done by directing a fine stream of water from a wash-bottle into the funnel, working downwards from the upper edges of the paper, and so washing the charcoal down into the apex of the filter (Fig. 3). Each washing must be allowed to drain right through before more water is used. This must be continued until the filtrate is entirely free from acid, which may be ascertained by allowing one or two drops of it to fall upon a piece of blue litmus paper.

In practice, the size of the filter should bear a rational relation to the quantity of *solid* matter to be separated from a liquid. This is more especially important when the material retained upon the filter has to be washed. If the amount of solid is small, the filter used should be proportionately small, and the washing operation will be more quickly and effectually accomplished than if an unduly large filter is employed.

FIG. 3.

2. **Solution.**—This term is applied both to the *act* of dissolving and to the *product obtained* by dissolving.

EXERCISE 2.—Place a little powdered potassium carbonate in a test-tube, and add a small quantity of water. In a few moments the salt will have entirely dissolved. The salt has undergone *solution* in water. The product is *a solution* of potassium carbonate. The water is called the *solvent*. The process of solution is

[1] In the following exercises, and in all analytical operations, distilled water must always be employed ; and when beakers, test-tubes, etc., are washed up after use, they must be finally rinsed with distilled water.

accelerated by heating the liquid, and it takes place more quickly the more finely the solid is powdered.

Put a similar quantity of potassium carbonate into another test-tube, and add a little dilute nitric acid. The salt again undergoes *solution*, the acid here being the solvent. But in this case there is a radical difference. First, a *visible* difference, in that the act of solution is accompanied by an effervescence, or rapid evolution of gas ; and second, an *invisible* difference ; for the resulting liquid *is not a solution of potassium carbonate, but of potassium nitrate.* In the first case, the process is not accompanied by any chemical change ; the operation is therefore called *simple solution* : the original substance is present in the liquid, and can be obtained in its former state by evaporating the water. In the second case, the process is distinguished as *chemical* solution, because chemical action took place between the substance dissolved and the solvent, and the original substance cannot be got back by evaporating the solvent.

3. **Evaporation.**—The process of changing from the liquid to the gaseous or vaporous state is known as *evaporation.* This operation is greatly accelerated by the application of heat.

FIG. 4.

When it takes place without the aid of external heat, the process is spoken of as *spontaneous evaporation.*

EXERCISE 3.—Pour the two solutions obtained in Exercise 2 into separate porcelain evaporating dishes, and heat them gently by means of a Bunsen with a "rose" burner (as shown in Fig. 4). Continue the operation until all the liquid has evaporated away and a dry residue is left. This is called *evaporating to dryness.* As the condition of *dryness* is approached, the flame must be turned down more and more, to prevent the substance from "sputtering." Try to conduct the operation so that as little as possible of the residue is lost in this way.

The two residues may now be examined by one simple test, which will prove that the one from the watery solution is the same as it was before being dissolved, and that the other is quite different. Add to each a few drops of dilute nitric acid : the first dissolves

with effervescence, as did the original potassium carbonate; the other is unacted on by the acid.

Sometimes it is necessary to carry on the operation of evaporation more carefully than can be done by heating the dish in the manner described. In this case the process is conducted upon a steam-bath. Water is boiled in a metal vessel (resembling a saucepan), and the evaporating-dish, supported by a metal ring which forms the cover, is heated by the steam. The following exercise is a case in point :—

EXERCISE 4.—Dissolve some crystals of ammonium nitrate in a little water; place half the solution in a dish, and evaporate it over a rose burner. Evaporate the other portion in a dish upon a steam-bath. Note the difference in the results in the two cases.

4. **Fusion** is the term used to denote the process of changing a substance from the solid to the liquid state by the action of heat. Thus, when lead is heated it *enters into a state of fusion*, or, shortly, it *fuses* or *melts*. Fusion must not be confounded with solution. Chemical action often takes place when one of the reacting substances is in a condition of *fusion*, which is incapable of taking place when they are only in *solution*. For example—

EXERCISE 5.—Dissolve a small piece of potassium hydroxide (*caustic potash*) in water, and add to the colourless solution a minute quantity of powdered manganese dioxide. No chemical action takes place.

Place a similar piece of potassium hydroxide in a dry test-tube, and heat it : the solid fuses to a colourless liquid. Drop into the fused mass a few particles of the manganese dioxide. Chemical action at once takes place, resulting in the formation of the deep green-coloured compound, potassium manganate. (This reaction is used as a test for manganese compounds.)

EXERCISE 6.—Place a *small* quantity of powdered barium sulphate in a test-tube, add water, and boil for a minute or two. If the amount of barium sulphate is *quite small*, it will be easy to *see* that practically none of it dissolves. Allow it to settle, and pour a few drops of the liquid upon a watch-glass, and set it to evaporate to dryness on a steam-bath.

Treat another similar quantity of the barium sulphate with dilute hydrochloric acid, and evaporate a few drops in the same

way. The result of these two operations will prove that *barium sulphate is insoluble in either water or hydrochloric acid.*

Next dissolve a little sodium carbonate in water, and add to the clear solution a few particles of barium sulphate; boil the liquid, and observe that no change takes place.

Now carefully mix a small quantity of barium sulphate with about five times as much sodium carbonate; place the powder in a platinum or nickel crucible, supported on a pipe-clay triangle in the manner shown in Fig. 5, and heat strongly with a blowpipe. When the mass has been in complete fusion for a few minutes, allow the crucible to cool. Then place it on its side in a small beaker with a little water, and warm gently. The mass in the crucible will soon become disintegrated, some of it dissolving, while a part remains undissolved. Filter the liquid as in Exercise 1, washing the residue upon the funnel until the filtrate no longer restores the blue colour to reddened litmus paper. Now pour a few drops of dilute hydrochloric acid upon the residue on the filter, receiving the liquid which passes through in a fresh beaker or test-tube. Observe that effervescence at once takes place. But this residue cannot be sodium carbonate, because that salt, being soluble in water, has been all removed; neither can it be barium sulphate, for that compound has been shown to be insoluble in dilute hydrochloric acid. By the process of fusion, the sodium carbonate and barium sulphate underwent a chemical reaction, resulting in the formation of sodium sulphate and barium carbonate. The former salt, being soluble in water, was dissolved in that liquid along with the excess of sodium carbonate. The barium carbonate is insoluble in water, but dissolves in dilute

FIG. 5.

hydrochloric acid, forming barium chloride (soluble) and carbon dioxide, which escapes as gas. Therefore, by fusion the *insoluble barium sulphate is converted into soluble barium carbonate.*

5. **Precipitation.**—When chemical action takes place between substances in solution, and one of the products of the action is insoluble, the latter substance is thrown out of solution, or *precipitated*. The substance so thrown down is termed a *precipitate*.

EXERCISE 7.—Dissolve a minute quantity of sodium chloride (common salt) in water in a test-tube. In another tube dissolve a small crystal of silver nitrate, and mix the two solutions together. The two compounds react upon each other, forming sodium nitrate (soluble in water) and silver chloride (insoluble in water). The insoluble white *precipitate* is therefore the silver chloride.

If, in the above example, the two substances are mixed in a *particular* proportion, there may have been *exactly* the amount of sodium chloride necessary to supply chlorine enough to unite with the *whole* of the silver in the silver nitrate used. In this case there would be nothing left in *solution* but sodium nitrate, *i.e.* no excess of either silver nitrate or of sodium chloride. Ascertain if this happened to be the case in Exercise 7, by the following experiment :—

EXERCISE 8.—Filter the mixture obtained above, and divide the filtrate into two portions. To one add a single drop of a solution of sodium chloride. (1) If a precipitate is formed, it proves that there is some silver nitrate present, and that therefore an *excess* of this compound was used in Exercise 7. Continue adding the sodium chloride solution one drop at a time,[1] shaking or stirring the liquid after every addition, so long as it produces further precipitation.

(2) If no precipitate is thrown down by adding sodium chloride, add *to the second portion of the filtrate* a single drop of silver nitrate solution. If this gives a precipitate, it proves that sodium chloride is present, and that therefore an *excess* of this substance had been employed in Exercise 7. Continue adding the silver solution drop by drop, with constant stirring, so as to hit off as

[1] When solutions are to be added drop by drop, it is best to use a pipette ; that is, a piece of ordinary glass tube drawn to a point at one end, and about 6 or 8 inches long.

nearly as possible the exact point when it just ceases to produce any further precipitate.

The exact point at which precipitation is complete is not equally easy to determine in all cases. Some precipitates are heavy, granular, or crystalline, and settle quickly; others again are light or flocculent, and only subside slowly and imperfectly, so that it is difficult to see whether the addition of more of one of the solutions does or does not produce any additional precipitate. In such cases the liquid should be filtered, and the filtrate tested by adding a few drops more of the precipitant.

Very often several substances present together in one and the same liquid form insoluble compounds with another which is added. These will not be all precipitated simultaneously, but in a certain order one after the other, the precipitation of one being more or less complete before that of the next begins. The substance being added, first select the compound present for which it has the greatest chemical affinity, and afterwards that with which it unites less eagerly. This being so, it will be evident that unless care be taken to ensure *complete* precipitation, it might easily happen that the *whole* of one of the substances present in the solution escaped precipitation. It is of the utmost importance, therefore, in analysis, to be quite sure that precipitation is as complete as possible. On the other hand, the reckless addition of precipitants is a fault which must be as carefully guarded against, as it is almost as fruitful a source of trouble as the other.

In most instances, also, it is essential to wash the precipitate until it is quite free from any of the soluble substances present in the liquid, as explained in Exercise 1. A precipitate may be removed from the filter either by means of a spatula (preferably platinum, but, failing this, either glass or porcelain; iron should never be used), or by pushing a glass rod through the apex of the filter, and then washing the precipitate through by means of the wash-bottle, or by dissolving it off by pouring into the funnel the liquid to be used for its solution. For example—

EXERCISE 9.—Add a solution of sodium carbonate to a solution of barium chloride, until precipitation is just complete. Barium

carbonate is precipitated, and sodium chloride remains in solution. Pour the mixture upon three separate filters, and wash the precipitate on each until quite free from sodium chloride (see Exercises 7 and 8), getting the precipitate well down into the apex.

Take the first filter, and remove a portion of the precipitate with a spatula. If the quantity in the funnel is small, then carefully draw the paper cone out of the funnel, spread it open upon a flat sheet of glass, and scrape off as much of the precipitate as possible with the spatula, and transfer it to a test-tube. Dissolve it by adding a few drops of hydrochloric acid.

Through the apex of the second filter push a glass rod, and wash the precipitate through into a test-tube, using a fine jet of water, and as little of it as possible. Dissolve this also by adding a few drops of the same acid.

Upon the third filter pour a small quantity of hydrochloric acid, collecting the filtrate in a test-tube. Pour the filtrate back over the precipitate once or twice, until the whole has dissolved.

6. **Ignition.**—Strictly speaking, this word carries with it the idea of combustion. In common speech it signifies the act of " setting fire " to an inflammable substance ; and in more scientific language we speak of the *ignition temperature,* or the *igniting-point* of a body, meaning thereby the temperature, to which it is necessary to raise it in order that combustion may be initiated. Unfortunately, in analytical phraseology the term *ignition* is used in a somewhat slipshod way to denote a variety of operations where substances are simply strongly heated, and where the idea of combustion is altogether excluded. In this book the words *heat* or *strongly heat* will be used instead of *ignite* to signify these operations.

EXERCISE 10. *Strongly heating in an open dish.*—Place a little solution of ammonium chloride in a small evaporating-dish, and evaporate to dryness. Then strongly heat the dish with the dry residue until no more white fumes (consisting of the volatilising ammonium chloride) are evolved. If the dish has been heated all over there should then be nothing left in it. The complete vaporisation of the salt is more quickly and certainly accomplished by using a small platinum capsule or crucible in which to heat the residue obtained by evaporating the solution to dryness.

EXERCISE 11. *Strongly heating in a tube closed at one end.*— Place a minute quantity of mercuric oxide in a small test-tube

(4 inches × $\frac{5}{16}$), and apply heat to the compound. Note the change of colour; also that it gradually disappears, and that a *sublimate* collects on the cool part of the tube, having a white metallic appearance. Test the evolved oxygen by means of a glowing splint of wood. By means of a paper "spill" rub the metallic sublimate, and (if necessary, with a pocket lens) see the globules of mercury.

EXERCISE 12. *Heating in the blowpipe flame.*—Select a piece of small tubing of *lead glass*, and heat it in a blowpipe flame, holding the glass in the *extreme tip* of the flame until it is red hot. Then gradually bring it further into the flame, and observe that when the glass reaches the *inner cone* of the flame a film begins to appear upon the red-hot portion. On withdrawing the glass to the tip of the flame again, this film gradually disappears. Bring the glass once more into the inner cone of flame, and when the film has again made its appearance, remove the glass and allow it to cool. It will then be seen that what appeared like a film when it was hot, is a black shining metallic-looking deposit in the glass. This deposit is *metallic lead.* The lead compound in the glass, when heated in the inner cone of flame, is *reduced* to the metallic state; and when, after being so reduced, it is heated in the tip of the flame (*i.e.* in the outer cone or sheath of the flame), the metal is again oxidised. The inner flame is therefore called the *reducing flame*, and the outer cone is distinguished as the *oxidising flame*.[1]

EXERCISE 13. *Heating on charcoal in the blowpipe flame.*—Select a close-grained piece of charcoal, as free as possible from cracks, and file a flat surface upon it with a broad, flat file.[2] On the flat part scoop a small hollow, and place in it a little red-lead mixed with about an equal quantity of sodium carbonate. Heat this mixture in the inner blowpipe flame, holding the blowpipe and the charcoal in the manner shown in Fig. 6, so that the flame shall play along the surface of the charcoal. Very quickly the lead oxide will be reduced to the metallic state, and appear in the form of brilliant silvery globules. When the charcoal is removed, it will be seen that surrounding the cavity there is a yellowish deposit, or

[1] The memory of the beginner may be aided by the alliteration, *O*uter, *O*xidising. The inner flame is a reducing agent by reason of the fact that within the cone there is an excess of strongly heated coal-gas; whereas in the outer flame there is an excess of heated atmospheric oxygen.

[2] Specially prepared rectangular blocks of charcoal (6 inches long and 1 square inch section) are sold for the purpose. One such block can be used many times.

incrustation. This consists of lead oxide. If the outer tip of the flame be directed upon this incrustation it will quickly disappear, and will impart a bluish colour to the end of the flame.

Pick out one or two of the globules of metal, and gently strike one with a small hammer, or with a pestle, upon some hard surface.
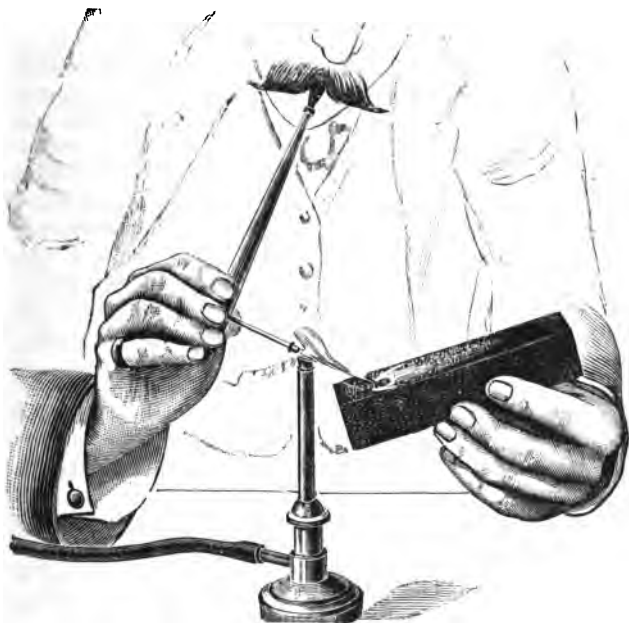
FIG. 6.

Note whether the metal is hard and brittle, or soft and malleable. Also further identify the metal as lead by rubbing it upon a piece of paper, which will be marked by it much as by an ordinary pencil.

EXERCISE 14.—Heat on another piece of charcoal a crystal or two of zinc sulphate with a little sodium carbonate in the inner blowpipe flame. No metallic globules are found in this case, because zinc is too easily oxidised ; but an incrustation appears on the charcoal, which is canary-yellow while hot, but turns white on cooling. Touch the incrustation with a single drop of a solution of cobalt nitrate, and again heat it, using the *outer* flame. The incrustation then becomes green. Notice that the incrustation is

not driven off by being thus heated, because zinc oxide is not volatile.

7. **Fusion with Borax.**—When borax is strongly heated, it melts to a clear vitreous mass. In this condition it is capable at a high temperature of dissolving many metallic compounds, giving in some cases characteristically coloured glasses.

EXERCISE 15.—Twist the end of a piece of platinum wire into a small round loop or eye,[1] and pick up a little borax upon it by first heating the wire and then dipping it while hot into the powdered salt. On heating the borax upon the wire in a blowpipe flame, it first swells up, and finally fuses, forming a transparent colourless bead of borax glass. Allow the bead to cool, and touch it with a glass rod which has been dipped into a solution of any cobalt salt, so as to bring only a minute quantity of the cobalt compound upon the bead. Heat the bead once more, and notice that as it melts the borax loses its transparent appearance. When again allowed to cool, the bead will appear of an azure blue colour.

If too much of the cobalt salt was employed, the bead may appear almost black ; in this case a part of it may be shaken off when it is fluid, and more borax picked up and melted with what remains of the original bead upon the wire. If too little cobalt is present, the colour will be correspondingly pale. The colour of the bead is best examined by holding it against a white object (such as the bottle of borax itself) in a good light.

Fuse the bead again, holding it first in the *outer* flame, and afterwards in the *inner* flame, and see that in each case when cold the blue colour remains the same.

FIG. 7.

[1] For greater convenience, as well as economy, a short piece of wire (about 2 inches) should be fixed into a glass tube, about the same length, to serve as a handle. The glass tube is first drawn out to a point, and the wire inserted into the fine end. On bringing this into a blowpipe flame, the glass fuses round the wire and holds it. Two or three of these should be made, and a convenient plan is to fit the glass tube into a cork, so that when not actually in use the wires can be kept in small test-tubes containing dilute hydrochloric acid, as in Fig. 7.

EXERCISE 16.—Make another borax bead, and touch it with a small quantity of solution of manganous sulphate. Heat this in the outer blowpipe flame. After cooling, examine the colour carefully: pale violet, lilac, purple, or amethyst. Heat the bead again, holding it in the inner flame. Notice that it gradually loses its opacity; that as it is heated, something in the fused mass which seems to give it an appearance of muddiness clears away, and the molten globule looks clear. When it is in this condition remove it, and when cold it will be found to have lost its colour entirely. Manganese compounds therefore give a purplish bead in the outer flame, which becomes colourless upon being heated in the reducing flame.

8. **Neutralisation.**—When an acid is carefully mixed with an alkali (the substances being in solution), a point is reached when the mixture no longer possesses the properties of either the acid or the alkali. The solution is then said to be *neutral.* The point of neutrality is ascertained by the use of certain sensitive colouring matters which have their colour changed by acids and alkalies. The commonest of these is *litmus*, the solution of which in water has a purple colour, capable of being turned *red* by acids, and *blue* by alkalies. The yellow colour of turmeric is changed to brown by alkalies, but is not altered by acids, therefore this can only be used to indicate alkalinity, and will not discriminate between a neutral and an acid liquid.

EXERCISE 17.—Add a few drops of litmus solution to a little dilute hydrochloric acid in a beaker standing upon a piece of white paper, or a white tile. Add to the red liquid some solution of sodium hydroxide, adding it cautiously in small quantities, with constant stirring, until the colour of the litmus is *just* turned blue. The liquid is now *alkaline.* By means of a glass rod moistened with the dilute acid, introduce a minute additional quantity of the acid, so as to cause the colour of the litmus to become of a purple tint. The solution is then *neutral,* and the least trace of either acid or alkali will at once turn it red or blue, as the case may be. (Instead of adding litmus solution, papers tinted with litmus may be dipped into the liquid.)

9. **Oxidation and Reduction.**—Processes which convert lower oxides (or compounds derived therefrom) into higher oxides of the same element (or compounds derived from them) are processes of oxidation. Thus, when either sulphur*ous* acid

or a sulph*ite* is converted into sulphu*ric* acid or a sulph*ate*, the processes is one of oxidation—

$$H_2SO_3 + O = H_2SO_4$$

Similarly, when ferrous sulphate is changed to ferric sulphate, we say that the iron in the ferrous salt has been oxidised—

$$2FeSO_4 + H_2SO_4 + O = H_2O + Fe_2(SO_4)_3$$

We say exactly the same, also, when ferrous chloride passes into ferric chloride, for although there is no oxygen in these compounds, the change is brought about by means of oxygen—

$$2FeCl_2 + 2HCl + O = H_2O + 2FeCl_3$$

Agents which bring about oxidation are termed *oxidising agents*, and those most frequently employed in qualitative analysis are *nitric acid, sodium peroxide*, and *chlorine*.

EXERCISE 18.—Make a solution of ferrous chloride by dissolving a few fragments of iron wire in strong hydrochloric acid in a test-tube, gently boiling the acid. To this solution add a few drops of nitric acid. Notice that the nearly colourless solution of ferrous chloride changes to the yellow ferric chloride, two molecules of nitric acid supplying three atoms of oxygen—

$$2HNO_3 = H_2O + 2NO + 3O$$
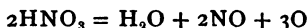
EXERCISE 19.—Dissolve a small crystal of chrome alum in cold water (this compound is a salt derived from chromium sesquioxide, Cr_2O_3). To this purple solution add a little sodium peroxide, and gently warm. The solution becomes bright yellow, owing to the formation of sodium chromate, a compound derived from the higher oxide, CrO_3.

Reduc⋯ ⟨t⟩he reverse process, namely, the withdrawal of oxygen, or ⋯ ⟨b⟩ivalent negative constituent, from a compound. Exercise 13 ⟩ ⟨e⟩xample of *reduction* by heating on charcoal. The commo⋯ ⟨r⟩educing agents employed in analysis for the reduction of ⟨s⟩ubstances in solution are *hydrogen, sulphurous acid*, and *stannous chloride*. Sulphuretted hydrogen, also, is a powerful reducing agent, although it is not often employed expressly for this purpose.

When metals such as iron, tin, or copper are dissolved in hydrochloric acid, the nascent hydrogen by its reducing

influence prevents the formation of the higher chlorides of the metals, and the compounds obtained are the ferrous, stannous, and cuprous chlorides respectively. The reducing action of nascent hydrogen may even go beyond the removal of oxygen or its equivalent; it sometimes itself unites with the element undergoing reduction. Nitric acid, for instance, may not only be reduced to the lower oxides of nitrogen, but can be further reduced to ammonia.

EXERCISE 20.—Place a little granulated zinc in a small beaker, cover it with water, and add a few drops of sulphuric acid so as to produce a *slow* evolution of hydrogen ; now add a little very dilute nitric acid, and notice that the evolution of hydrogen becomes much slower—with a little care it can be made to cease altogether. The nascent hydrogen is attacking the nitric acid and *reducing* it to ammonia, which unites with the sulphuric acid present, forming ammonium sulphate. After about a quarter of an hour take a little of the liquid in a test-tube, add sodium hydroxide, and warm ; ammonia will be evolved, which may be detected by its smell or its action on red litmus paper.

A similar action takes place when nascent hydrogen acts upon arsenious oxide. This compound is reduced first to elemental arsenic, and then still further reduced to arsine, AsH_3.

EXERCISE 21.—To a solution of mercuric chloride, add a little stannous chloride. A white precipitate is first obtained consisting of mercur*ous* chloride. If the mixture be now gently warmed the white precipitate turns grey, owing to its further reduction to metallic mercury.

$$(1)\ 2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
$$(2)\ Hg_2Cl_2 + SnCl_2 = 2Hg\ \ \ + SnCl_4$$
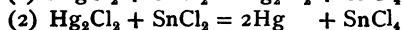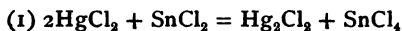
CHAPTER II

ANALYTICAL CLASSIFICATION

The word *analysis*, in its strict meaning, signifies the breaking up or separation of a compound substance into its constituent parts. It is the true antithesis of the word *synthesis*, which means the building up of a compound from its constituents. For example, when an electric current is passed through a solution of common salt, the compound is separated into its two component elements, sodium and chlorine. The operation is therefore "analytical." When sodium and chlorine are brought together under suitable conditions, the two elements unite, and reproduce the compound sodium chloride, the process in this case being a synthetical one.

But the word *analysis* has come to bear a wider meaning, and to include all the various processes and operations which chemists make use of in order to find out what any compound is composed of, or to enable them to identify the substance, quite irrespective of whether or not the process involves the breaking up of the body into its component parts. Thus, a chemist will often recognise a substance by its particular crystalline form, or from some other characteristic appearance it may present when examined under a miscroscope (*microscopic analysis*). Or sometimes he can detect the presence of certain elements in an unknown substance, by examining the light which is emitted when the compound is strongly heated (*spectrum analysis*).

Reactions.—Most analytical operations, however, involve some chemical change. These changes are called *reactions*. When the change is effected by strongly heating the substance, it is described as a *dry reaction*, or a *reaction in the dry way.*

This is to distinguish this class of reactions from those which take place between substances that are dissolved, either in water or some other liquid, and which are sometimes spoken of as *wet reactions,* or *reactions in the wet way.*

Most analytical reactions are " double decompositions," in which one of the products of the chemical action is either markedly different from the others and from the reacting compounds, in its solubility, or its colour; or where it is evolved as a gas having properties by which it may be readily identified. For instance, the two compounds barium chloride and sodium sulphate are soluble in water, forming colourless solutions; if these are mixed together, " double decomposition " takes place, resulting in the formation of sodium chloride and barium sulphate thus—

$$BaCl_2 + Na_2SO_4 = 2NaCl + BaSO_4$$
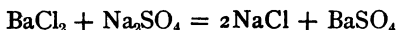
The barium sulphate is practically insoluble in water, and consequently is precipitated. Now, if we know some property belonging to this precipitate of barium sulphate which is so characteristic of the compound that we could thereby identify it and distinguish it from all other white precipitates, then this reaction between barium chloride and sodium sulphate can obviously be used as a means of testing for the presence of either a soluble *barium* salt or a soluble *sulphate.* For if, on adding a solution of sodium sulphate to an *unknown* solution, barium sulphate were precipitated, the unknown liquid must have contained a soluble barium salt; or, on the other hand, if we add barium chloride to an unknown solution and obtain barium sulphate again, then this unknown solution must have contained a sulphate.[1]

Reagents.—The materials that are used to bring about analytical reactions are called *reagents.* Thus in the illustration given above, the sodium sulphate is the *reagent* when it is added to the unknown solution in order to test for barium; while the barium chloride is the *reagent* when it is used to test for a sulphate. Some reagents are capable of causing reactions of a similar character with a number of substances; such are

[1] Sulphuric acid being included, as hydrogen sulphate.

c

often known as *general* reagents. Others, again, are employed because they produce a characteristic reaction with some one substance in particular; these are distinguished as *special* reagents.

Reagents are the tools with which the analyst works, and upon the intelligent and skilful use of them everything depends.

Analytical Classification.—Substances are usually divided into two classes, namely, (1) *Metals*, and (2) *Acid-radicals*. These are also sometimes called *positive* radicals and *negative* radicals respectively. When analysing such a compound as sodium chloride, NaCl, the sodium and the chlorine are each separately detected : the sodium is the metal (or positive radical), and the chlorine is the acid (or negative) radical. But in such a case as sodium nitrate, $NaNO_3$, we do not separately detect the sodium, the nitrogen, and the oxygen, but the sodium and the negative or acid radical represented by the formula NO_3. Or, again, when such a compound as ammonium sulphate, $(NH_4)_2SO_4$, is submitted to analysis, we do not separately test for the elements nitrogen, hydrogen, sulphur, and oxygen, but for the positive radical NH_4, and the acid radical SO_4.

Sometimes the radicals, whether metals or acid-radicals, may be detected by being actually isolated, in which case they are recognised by their known properties in the free state. For example, from the compound lead chloride, $PbCl_2$, it is easy to isolate both the lead and the chlorine. The metal lead so obtained is readily identified by its familiar physical properties, while the gas chlorine is equally easily distinguished by its own well-known characteristics.

In some cases, where a radical cannot be isolated, it may be detected by the separation of some product of its decomposition. Thus, in such a compound as ammonium carbonate, $(NH_4)_2CO_3$, neither the positive radical NH_4, nor the acid-radical CO_3 can be isolated, but we detect the presence of the former by the evolution of ammonia, NH_3, and the latter by the expulsion of carbon dioxide, CO_2, from the compound.

In the large majority of cases, however, whether the various radicals are capable of isolated existence or not, they are detected by causing them to pass into fresh combinations

with certain reagents, whereby new compounds are formed, which are readily recognised by their known properties. Thus, in the case of sodium chloride above quoted, instead of isolating the chlorine, we can employ the reagent silver nitrate, $AgNO_3$. When this is added to a solution of sodium chloride, double decomposition takes place, and silver chloride, AgCl, is formed, which, being insoluble in water, is precipitated. Silver chloride has properties by which it is easily recognised, hence by the formation of this compound we can detect the presence of the chlorine in sodium chloride.

In all such cases as these the interaction is between the *ions* into which the compounds dissociate when dissolved in water. A solution of sodium chloride, for example, contains $\overset{+}{Na}$ and $\overset{-}{Cl}$ ions ; the silver nitrate contains $\overset{+}{Ag}$ and $\overset{-}{NO_3}$ ions. When these solutions are mixed, the positive silver ions unite with the negative chlorine ions to produce the electrically neutral and insoluble silver chloride, which therefore separates out. The silver ions, therefore, are the test for chlorine ions, and *vice versâ* chlorine ions are the reagents for detecting silver ions. Any chlorine compound which on dissociation furnishes chlorine ions, will therefore respond to this test with silver ions. There are, however, many compounds containing chlorine which give no precipitate of silver chloride on the addition of silver nitrate. Familiar among these are the chlorates and perchlorates. These compounds dissociate on solution, not into simple chlorine ions, but into the complex $\overset{-}{ClO_3}$ and $\overset{-}{ClO_4}$ ions. Such solutions, therefore, contain no $\overset{-}{Cl}$ ions, and are therefore incapable of forming AgCl with $\overset{+}{Ag}$ ions.

In analytical classification the metallic or positive radicals are classified into groups, based upon their behaviour towards certain chosen reagents, known as *group-reagents* or *general-reagents*, which are used in a certain order. ·

Group I. (*hydrochloric acid group*).—Metals whose chlorides are precipitated by dilute hydrochloric acid.

Group II. (*sulphuretted hydrogen group*).—Metals whose sulphides are precipitated from *acid* solutions by sulphuretted hydrogen.

Group IIIA. (*ammonia group*).—Metals whose hydroxides are precipitated by ammonia in presence of ammonium chloride.

Group IIIB. (*ammonium sulphide group*).—Metals whose sulphides are precipitated by ammonium sulphide in presence of ammonia.

Group IV. (*ammonium carbonate group*).—Metals whose carbonates are precipitated by ammonium carbonate in presence of ammonium chloride.

Group V. (no group-reagent).—Metals which are not precipitated by any of the above reagents.

Group I.	Group II.	Group IIIA.	Group IIIB.	Group IV.	Group V.
Lead [1] Silver Mercury (ous)	Lead [1] Mercury(ic) Copper Bismuth Cadmium Arsenic Antimony Tin	Aluminium Chromium Iron	Manganese Zinc Nickel Cobalt	Barium Strontium Calcium	Magnesium Sodium Potassium Ammonium

The *order* in which the group-agents are used is an indispensable condition of this classification. They can only be employed in the order in which the groups are here numbered, for the reason that each is only capable of separating its own particular group from *those groups which follow*, and not from those which go before. For example, if the metals of Group I. are not first removed by precipitation with hydrochloric acid before the group-reagent for Group II. is added, they would all be precipitated as sulphides along with the metals of Group II., and thus no separation would be effected. There are conditions under which the group-reagent for Group IIIA. fails to separate this group from those which follow. When these conditions are present, a special procedure has to be adopted, which will be explained in its proper place later on.

[1] The reason why lead is placed in both Groups I. and II. is explained under the reactions for that metal.

CHAPTER III

REACTIONS OF THE METALS OF GROUP V

THIS group contains the alkali metals (ammonium being regarded as a metal), and also the element magnesium, which is more nearly allied to the metals of the *alkaline earths*. The members of this family are not precipitated by any group-reagent, but they are (with the exception of ammonium) separately tested for in the solution which is obtained after the metals of Groups I. to IV. have been removed. By referring to the classification table, it will be seen that, in the course of separating the various groups, certain ammonium compounds are employed, therefore it will be obvious that it is necessary to test for this "metal" in the substance under examination *before* adding any ammoniacal compounds.

Ammonium, NH_4

DRY REACTIONS.—When heated alone in a glass tube, ammonium salts undergo change.

(*a*) If the acid is readily volatile (*e.g.* hydrochloric acid), the salt dissociates, but the ammonia and the volatile acid, as they together pass away from the heated area, immediately reunite, reproducing the original compound, which then settles or condenses on the cool part of the tube, forming a *sublimate*.

(*b*) If the acid is non-volatile, or volatile only at a high temperature (*e.g.* sulphuric or phosphoric), then the ammonium salt is decomposed, ammonia being evolved, while the acid remains.

(*c*) The ammonium salts of certain oxyacids which readily part with oxygen (such as ammonium nitrate, nitrite, chromate)

are also decomposed by heat, the ammonia being oxidised to nitrogen or oxides of nitrogen.

$$NH_4NO_3 = 2H_2O + N_2O$$
$$NH_4NO_2 = 2H_2O + N_2$$
$$(NH_4)_2Cr_2O_7 = Cr_2O_3 + 4H_2O + N_2$$
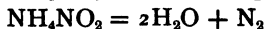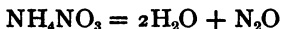
Ammonium is separated from the other members of the group by evaporating the solution to dryness, and strongly heating the residue until the ammonia is completely expelled, which may generally be regarded as accomplished when fumes are no longer given off.

WET REACTIONS.—Ammonium salts are all soluble in water, therefore it is only in concentrated solutions that any precipitations with reagents can be formed.

Caustic alkalies (NaHO or KHO) and oxides or hydroxides of metals of the alkaline earths (*e.g.* CaO, Ba(HO)$_2$), when heated with an ammonium salt, cause the evolution of ammonia gas, NH$_3$.

$$(NH_4)_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O + 2NH_3$$
$$2NH_4Cl + CaO = CaCl_2 + H_2O + 2NH_3$$
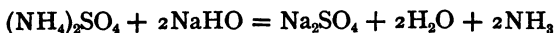
In practice, sodium hydroxide solution is added either to the solid salt or to its solution in water, and the mixture gently warmed. The evolved ammonia may be recognised (1) by its characteristic odour if present in sufficient quantities; (2) by its power of restoring the blue colour to moist reddened litmus paper, or of turning turmeric paper brown; (3) by the formation of white fumes when a glass rod moistened with strong hydrochloric acid is held in the mouth of the test-tube.

Sodium, Na

DRY REACTION.—Sodium compounds, when heated upon a platinum wire in a Bunsen flame, undergo volatilisation, and impart to the flame a brilliant golden yellow colour. This flame-reaction is the most characteristic and delicate test for this metal.

WET REACTIONS.—All sodium salts are soluble; sodium

platino-chloride is soluble in water, in alcohol, and in ether. Hydrogen sodium tartrate also is freely soluble in water. Sodium pyroantimonate, however, is less soluble in water than the corresponding potassium salt, and is therefore precipitated by the addition of a strong solution of potassium pyroanti-monate to a strong solution of a sodium salt, such as sodium chloride, thus—

$$H_2K_2Sb_2O_7 + 2NaCl = H_2Na_2Sb_2O_7 + 2KCl$$
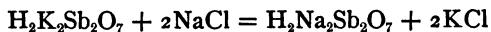
Potassium, K

DRY REACTION.—When potassium compounds are heated upon a platinum wire in a Bunsen flame, they impart to the flame a pale violet or lilac colour. This delicate tint, however, is completely masked by the intense yellow colour which the presence of even minute quantities of sodium compounds impart to the flame.

Introduce a fragment of potassium nitrate into the Bunsen flame upon a loop of clean platinum wire ;[1] notice the lilac colour imparted to the flame. Now look at the flame through a *potassioscope*,[2] and observe that it appears a brilliant crimson-red colour. Upon another wire introduce a particle of sodium chloride into the flame, and notice that when this is examined through the potassioscope, the intense golden-yellow light is absolutely cut off, and is invisible. Now touch the wire containing the nitre with a fragment of sodium chloride, and again bring it into the flame. The yellow of the sodium completely overpowers and masks the violet of the potassium when viewed direct, but if looked at through the

[1] By merely touching the wire with the fingers, it contracts sufficient sodium compounds to give the yellow flame. To clean it, it should be dipped in hydrochloric acid and heated until it ceases to impart any colour to the flame.

[2] The potassioscope consists merely of a small flat glass cell, containing a dilute solution of one of the aniline blue dyes, known as "Soluble Blue X. L." The advantage of this over ordinary blue glass or the older *indigo prism* lies in the fact that *no other metal but potassium* (except the extremely rare element rubidium) gives a flame which appears red when viewed through the potassioscope, whereas lithium, barium, strontium, and calcium all give flames which appear red through indigo or blue glass.

potassioscope, the red colour due to the potassium shines up as brilliantly as before, while the yellow is completely intercepted.[1]

WET REACTIONS.—Most potassium salts are soluble in water. *Use a solution of potassium chloride.*

Platinum chloride,[2] $PtCl_4$, produces, with concentrated solutions of potassium salts, a yellow crystalline precipitate of potassium chloro-platinate (or *potassium platinic chloride*), K_2PtCl_6, soluble in 110 parts of water at 10° (therefore more soluble than the corresponding ammonium compound). Soluble in alkalies (therefore the solutions used should be acid); nearly insoluble in alcohol; quite insoluble in a mixture of alcohol and ether (therefore the precipitation of this compound is promoted by the addition of alcohol).

Hydrogen sodium tartrate, $HNa(C_4H_4O_6)$, gives, with solutions of potassium salts, a white crystalline precipitate of hydrogen potassium tartrate, $HK(C_4H_4O_6)$; soluble in much water, and also in acids and alkalies (therefore the solution should be both concentrated and neutral). The precipitate is insoluble in alcohol.
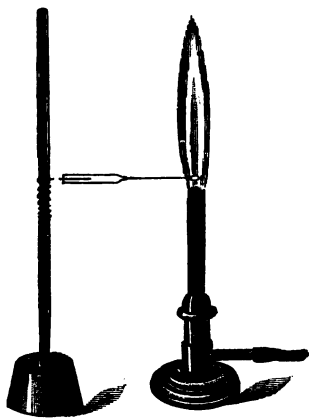
FIG. 8.

[1] When studying flame reactions, it is often of the greatest convenience to use a stand on which to support the platinum wire, so that the hands may be free; a simple stand is readily constructed as shown in Fig. 8. A piece of glass tube or glass rod is inserted in a large cork (rubber, being heavier, makes a steadier foot), and a piece of galvanized iron wire is twisted two or three times round the rod with one end projecting at right angles to the upright. The little glass tube into which the platinum wire is fused is then slipped over the projecting iron wire. This arrangement admits of the wire being raised or lowered as desired, while at the same time it readily remains in any position.

[2] In reality the reagent used is chloroplatinic acid, H_2PtCl_6, which by long habit is called platinum chloride: it is platinum chloride $PtCl_4$ plus two molecules of hydrochloric acid, $PtCl_4$, $2HCl$.

Hydrofluosilicic acid (or silico-fluoric acid), H_2SiF_6, throws down a white precipitate of gelatinous appearance, consisting of potassium silicofluoride, K_2SiF_6, sparingly soluble in water.

Magnesium, Mg

DRY REACTION.—When magnesium salts are strongly heated in the outer blowpipe, a white infusible residue of the oxide is left. If, after cooling, the residue be moistened with a drop or two of cobalt nitrate solution and again strongly heated in the outer blowpipe flame, the mass acquires a pink colour. This reaction is reliable only in the absence of other metallic oxides.

WET REACTIONS.—Of the common salts of magnesium, the sulphate, chromate, nitrate, and halogen salts are soluble in water. One prominent characteristic of magnesium compounds is the readiness with which they form " double " salts, many of which are soluble in water. *Use magnesium sulphate.*

Alkaline hydroxides (NH_4HO, KHO, $NaHO$, $Ca(HO)_2$, or $Ba(HO)_2$) precipitate from solutions of magnesium sulphate or chloride, white magnesium hydroxide, $Mg(HO)_2$. Almost insoluble in water; soluble in acids, soluble in ammonium chloride—

$$Mg(HO)_2 + 4NH_4Cl = 2NH_4HO + MgCl_2,2NH_4Cl \text{ (soluble double salt)}$$

Owing to the solubility of magnesium hydroxide in ammonium chloride, only half the magnesium is precipitated from magnesium chloride by means of ammonia, thus—

$$2MgCl_2 + 2NH_4HO = Mg(HO)_2 + MgCl_2,2NH_4Cl$$

If ammonium chloride is previously present in sufficient quantity to combine with the whole of the magnesium hydroxide, the alkaline hydroxides give no precipitate.

Alkaline carbonates (K_2CO_3, Na_2CO_3, $(NH_4)_2CO_3$) produce in solutions of magnesium salts, in the absence of ammonium salts, precipitates of basic carbonates of magnesium, the composition of which varies with conditions of temperature

and concentration. The precipitate with $(NH_4)_2CO_3$ only separates out after a short time. *In the presence of ammonium chloride these reagents give no precipitate.*

Hydrogen disodium phosphate, HNa_2PO_4, precipitates hydrogen magnesium phosphate, $HMgPO_4$, and tri-magnesium phosphate, $Mg_3(PO_4)_2$. In the presence of ammonium chloride, however, the double ammonium magnesium phosphate is thrown down as a white crystalline precipitate, NH_4MgPO_4. It is appreciably soluble in water, but *insoluble in ammonia;* hence ammonia must be previously added.

In very dilute solutions the precipitation only takes place on long standing. It is accelerated by stirring with a glass rod, the deposition first appearing where the rod has rubbed the glass vessel. The precipitate is soluble in acids, even acetic acid, but reprecipitated by ammonia.

A solution is examined for metals of Group V. by Table V. on the page following.

TABLE V

DETECTION OF THE METALS OF GROUP V

| A. To a small portion add NaHO, and heat.[1] The evolution of NH$_3$ (detected by its smell, and action on test papers) indicates

Presence NH$_4$. | B. To a second portion add NH$_4$Cl, NH$_4$HO, and HNa$_2$PO$_4$. A white crystalline precipitate of NH$_4$MgPO$_4$.

Presence Mg. | C. Evaporate the main portion to dryness. Expel all ammonium salts by strongly heating the residue on platinum foil until all fuming ceases. Test residue on clean platinum wire in flame. Intense yellow flame.

Presence Na.

A red flame when seen through the potassioscope.

Presence K.

Conformation of potassium may be made by dissolving the residue in two drops of water, adding one drop HCl, and a few drops H$_2$PtCl$_6$. A yellow crystalline precipitate of K$_2$PtCl$_6$. |

[1] In a *complete* analysis ammonium salts are always present here, having been introduced in the process of separating the other groups. This test for ammonium compounds, therefore, must be applied to the original substance under analysis before ammoniacal reagents have been added.

CHAPTER IV

REACTIONS OF THE METALS OF GROUP IV

Barium, Ba

Dry Reaction.—Barium compounds, heated on platinum wire in the Bunsen flame, impart a pale apple-green colour to the flame, which becomes more distinct if the substance on the wire is moistened with strong hydrochloric acid. The test is not very reliable except as a confirmatory test.

Barium sulphate, $BaSO_4$ (also $SrSO_4$ and $CaSO_4$), when heated on charcoal or with carbon, is reduced to the sulphide.

Wet Reactions.—Of the common salts of barium, the chloride, bromide, iodide, nitrate, chlorate, acetate, and sulphide are soluble in water.

Ammonium carbonate, $(NH_4)_2CO_3$, group-reagent (also Na_2CO_3 and K_2CO_3), precipitates barium carbonate, $BaCO_3$, as a white amorphous powder. Insoluble in water; readily dissolved, with evolution of carbon dioxide, by dilute acids; *slightly soluble* in NH_4Cl.

H_2SO_4, or any soluble sulphate, produces a white granular precipitate of $BaSO_4$, practically insoluble in water, insoluble also in acids and alkalies (except by prolonged boiling with strong acids and concentrated sodium carbonate, when it is slowly dissolved). Insoluble in solutions of $(NH_4)_2SO_4$.

$BaSO_4$, being practically insoluble in water, is precipitated by a saturated solution of $SrSO_4$, although such a solution contains only 1 part salt in 7000 parts of water.

Potassium chromate, K_2CrO_4, produces a primrose-yellow precipitate of barium chromate, $BaCrO_4$. It is insoluble in acetic acid (*distinction from* $SrCrO_4$); soluble in HNO_3 and in HCl.

Hydrofluosilicic acid, H_2SiF_6, gives a white crystalline precipitate of barium silicofluoride, $BaSiF_6$, slightly soluble in water, but insoluble on the addition of alcohol.

Strontium, Sr

DRY REACTION.—When heated in the Bunsen flame, volatile strontium salts, such as $SrCl_2$, $Sr(NO_3)_2$, impart a rich crimson colour to the flame; other salts require to be moistened upon the wire with strong HCl.

WET REACTIONS.—The same common salts of strontium as of barium are soluble in water. The chromate and sulphate are somewhat soluble.

$(NH_4)_2CO_3$ (Na_2CO_3 and K_2CO_3) precipitates $SrCO_3$, exactly similar to the barium compound in its reactions.

H_2SO_4 or soluble sulphates precipitate $SrSO_4$. The precipitate is slightly soluble in water but almost insoluble in a solution of $(NH_4)_2SO_4$ (*distinction from* $CaSO_4$). $SrSO_4$ is precipitated by a solution of $CaSO_4$; the precipitation does not take place *at once* in cold solutions, but appears quickly on heating.

Calcium, Ca

DRY REACTIONS.—Calcium compounds, when heated in a Bunsen flame, impart to it a reddish colour, especially if previously moistened with hydrochloric acid. The presence of strontium masks the red colour given by calcium compounds.

WET REACTIONS.—The same common salts of calcium are soluble in water as of strontium and barium.

$(NH_4)_2CO_3$ (also Na_2CO_3 and K_2CO_3) precipitates $CaCO_3$, similar to the barium and strontium compounds in its reactions.

H_2SO_4 added to a *strong* solution of a calcium salt give an *immediate* precipitate of calcium sulphate. From more dilute solutions the precipitate only separates after some time, or, if still more dilute, not at all. The precipitate is insoluble in alcohol, therefore the addition of this liquid in considerable bulk favours the precipitation.

Calcium sulphate is readily soluble in a concentrated

solution of ammonium sulphate, especially when hot (*distinction from* $SrSO_4$ *and* $BaSO_4$). Boiling with potassium carbonate easily converts it into calcium carbonate.

Ammonium oxalate, $(NH_4)_2C_2O_4$, gives a white crystalline precipitate of calcium oxalate. The precipitate is soluble in mineral acids, but insoluble in acetic acid and in ammonia.

SEPARATION OF GROUPS IV. AND V

The solution is first rendered alkaline by the addition of NH_4HO. NH_4Cl is then added (to prevent the precipitation of magnesium carbonate), after which ammonium carbonate is added until the carbonates of the metals of Group IV. are completely thrown down. The mixture may be gently warmed. [It must not be boiled, or the precipitated carbonates will react with the NH_4Cl, forming soluble chlorides, while NH_3 and CO_2 will escape with the steam; thus, $BaCO_3 + 2NH_4Cl = BaCl_2 + CO_2 + 2NH_3 + H_2O$.] The mixture is filtered. The filtrate is examined for the metals of Group V. by the table given on p. 27, while the precipitate is examined by Table IV. on the opposite page.

TABLE IV

SEPARATION OF THE METALS OF GROUP IV

The precipitate, consisting of $BaCO_3$, $SrCO_3$, and $CaCO_3$, is washed, and then dissolved in a small quantity of warm dilute acetic acid, $H(C_2H_3O_2)$. To the solution thus obtained potassium chromate, K_2CrO_4, is added; the mixture gently warmed and filtered.[1]		
The precipitate consists of yellow barium chromate, $BaCrO_4$.	The filtrate contains strontium and calcium acetates. Add a strong solution of $(NH_4)_2SO_4$, and boil for a short time to ensure the solution of $CaSO_4$. Filter.	
Boil the precipitate with K_2CO_3, which converts $BaCrO_4$ into $BaCO_3$. Filter, and wash the precipitate free from the K_2CrO_4. Dissolve the precipitate in HCl, and confirm by $SrSO_4$ or H_2SiF_6.	The precipitate consists of $SrSO_4$. Wash the precipitate thoroughly, and confirm by the flame reaction.	The solution contains calcium sulphate. Add ammonium oxalate $(NH_4)_2C_2O_4$ (or $(NH_4)HO$ and oxalic acid, $H_2C_2O_4$). A white precipitate of CaC_2O_4 confirms calcium.

[1] Instead of adding the chromate at once to the whole of the solution, a small separate portion may be used, and the presence or absence of the Ba thus ascertained. If *present*, then the whole of the solution is treated as above, and the precipitation of barium chromate may then be taken as confirmatory. If *absent*, then a second small portion of the solution is taken, and tested for Sr by adding $CaSO_4$. If Sr is present, then the separation of Sr and Ca is carried out as shown above; but if $CaSO_4$ gives no precipitate even on warming, thus proving the absence of Sr, the remainder of the solution is at once tested for Ca by the oxalate reaction.

CHAPTER V

Aluminium, Al

DRY REACTION.—When aluminium compounds are strongly heated on charcoal in the outer flame, aluminium oxide is formed, and if this be moistened with a solution of cobalt nitrate, and again strongly heated, either upon the charcoal or upon a loop of platinum wire, the mass assumes a rich blue colour, due to the formation of cobalt aluminate.

This test is, however, greatly masked if other metallic oxides which are coloured are present at the same time. It may be employed as a confirmatory test when aluminium is separated from iron and chromium in the course of analysis.

WET REACTIONS.—Of the common salts of aluminium, the chloride, Al_2Cl_6, and sulphate, $Al_2(SO_4)_3$, are soluble in water. The important salts, however, are the double sulphates of aluminium with ammonium or potassium, known as *ammonium alum*, $(NH_4)_2SO_4,Al_2(SO_4)_3,24H_2O$, and *potassium alum*, $K_2SO_4,Al_2(SO_4)_3,24H_2O$, respectively. A solution of either of these alums may be used for the following reactions.

NH₄HO throws down a white translucent precipitate of aluminum hydroxide, or $Al_2(HO)_6$. Soluble in a large excess of the reagent, but on gently boiling, the hydroxide is entirely precipitated. In the presence of ammonium chloride, the precipitation by ammonia is complete. The precipitate is readily soluble in mineral acids, and in acetic acid.

KHO or **NaHO** produces the same precipitate, which readily combines with an excess of the reagent, forming a soluble

aluminate of potassium or sodium ($Al_2O_3,3Na_2O$ or $Na_6Al_2O_6$). These aluminates are decomposed by acids—

$$Al_2O_3,3Na_2O + 6HCl = Al_2(HO)_6 + 6NaCl$$
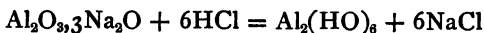
but any excess of the acid beyond that required to combine with the sodium of the aluminate at once re-dissolves the $Al_2(HO)_6$.

BaCO₃ suspended in water, precipitates $Al_2(HO)_6$, carbon dioxide being evolved. The precipitation is complete even in the cold.[1] If alum or aluminium sulphate is used, the precipitate is mixed with insoluble barium sulphate—

$$Al_2(SO_4)_3 + 3BaCO_3 + 3H_2O = Al_2(HO)_6 + 3BaSO_4 + 3CO_2$$

(NH₄)₂S precipitates aluminium hydroxide, with evolution of sulphuretted hydrogen (compare Fe)—

$$Al_2(SO_4)_3 + 3(NH_4)_2S + 6H_2O = Al_2(HO)_6 + 3(NH_4)_2SO_4 + 3H_2S$$
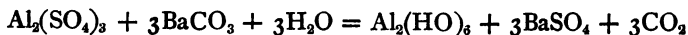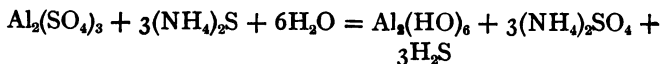
[Aluminium forms no sulphide in the wet way. Al_2S_3 (obtained by the union of Al and S) is decomposed instantly by water, forming the trioxide, and evolving H_2S.]

Chromium, Cr

DRY REACTIONS. — Chromium compounds impart to a borax bead a grass-green colour, when heated either in the outer or inner blowpipe flame.

When fused in a platinum capsule with five or six times their weight of a mixture consisting of 1 part of KNO_3 and 2 parts of dry Na_2CO_3 or K_2CO_3 (or 1 part of $KClO_3$ with 6 parts of Na_2CO_3), chromium compounds are converted into alkaline chromates, which appear as *a yellow mass, soluble in water to a yellow solution.* In the case of chromic oxide, for instance, Cr_2O_3, the reaction is the following :—

$$Cr_2O_3 + 2K_2CO_3 + KClO_3 = 2K_2CrO_4 + KCl + 2CO$$
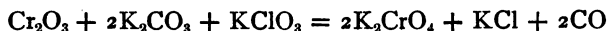
[1] In the presence of certain organic acids, as oxalic, tartaric, or citric acids, aluminium hydroxide is only more or less imperfectly precipitated by the above-mentioned reagents, owing to the formation of soluble double salts of the organic acid with aluminium and the alkali metal ; such, for example, as the double tartrate of aluminium and sodium, $Na_2(C_4H_4O_6),Al_2(C_4H_4O_6)_3$. This applies also in the case of the corresponding chromium and iron compounds.

WET REACTIONS.—Two classes of chromium compounds will be considered, namely the *chromic* compounds, derived from chromium sesquioxide, Cr_2O_3; and the *chromates*, derived from chromium trioxide (or chromic anhydride), CrO_3.

a. Chromic Salts.—These salts are mostly of a purplish or violet-grey colour when solid, giving either a purple or green solution when dissolved.

NH₄HO produces a bluish or greenish-grey precipitate of chromic hydroxide, $Cr_2(HO)_6$, partially dissolved by excess of ammonia in the cold, giving a lilac-coloured liquid, but completely precipitated on gently boiling. $Cr_2(HO)_6$ is readily soluble in acids.

KHO and NaHO precipitate $Cr_2(HO)_6$, readily soluble in excess, giving a deep green solution. Reprecipitated by neutralisation with HCl, and by boiling with NH₄Cl, as in the case of Al.

BaCO₃ precipitates a mixture of the hydroxide and basic carbonate. Complete precipitation only after some hours.

K₂CO₃ and Na₂CO₃ gave a similar precipitate, the composition of which varies with the conditions of precipitation.

(NH₄)₂S precipitates $Cr_2(HO)_6$. Precipitation complete. [Cr, like Al, is incapable of forming a sulphide in the wet way.]

Oxidation of Chromic Compounds.—By means of suitable oxidising agents, chromic compounds are readily converted into compounds of chromic acid, the mechanism of the change in all cases being the oxidation of the sesquioxide into the trioxide; thus—

$$Cr_2O_3 + 3O = 2CrO_3$$
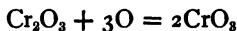
One method, namely, by fusion with oxidising agents, has been explained under *Dry Reactions*. The Cr_2O_3 in that instance is oxidised into the potassium salt of chromic acid. The oxidation may be accomplished in the wet way—

(1) By the action of hypochlorites (or hypobromites) in the presence of caustic alkalies, either employed as such, or formed in the solution by the use of chlorine or bromine in the presence of the caustic alkali—

$$Cr_2(HO)_6 + 4KHO + 3KClO = 3KCl + 2K_2CrO_4 + 5H_2O$$
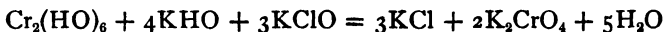
(2) **By the action of sodium peroxide.** If a small quantity of Na_2O_2 be added to chromium hydroxide suspended in water, and the mixture gently warmed, the chromium compound is immediately converted into the yellow sodium chromate; thus—

$$Cr_2(HO)_6 + 3Na_2O_2 = 2Na_2CrO_4 + 2NaHO + 2H_2O$$

β. **Chromic Acid and Chromates.**—The acid, H_2CrO_4, has never been isolated. The anhydride, CrO_3, is readily obtained by adding strong H_2SO_4 to a cold strong solution of potassium dichromate, when the oxide is deposited in the form of red silky needles. It forms two classes of salts, viz. the normal chromates, of which K_2CrO_4 is a type; and the dichromates, of which $K_2Cr_2O_7$ is a familiar example. The salts are mostly yellow or red in colour. Both the chromates and dichromates of the alkalies are soluble in water. The former (yellow) are converted into the latter (red) by the addition of the requisite amount of sulphuric acid—

$$2K_2CrO_4 + H_2SO_4 = K_2Cr_2O_7 + K_2SO_4 + H_2O$$

The most important of the insoluble chromates made use of in analysis, and which are all precipitated by the addition of potassium chromate to solutions of the metallic salts, are the following :—

Barium chromate, $BaCrO_4$ (see Ba reactions, p. 28).

Lead chromate, $PbCrO_4$ (see Pb reactions, p. 58).—$PbCrO_4$ melts without decomposition, and solidifies on cooling to a brown crystalline mass. At higher temperatures it gives off oxgen—

$$2PbCrO_4 = Cr_2O_3 + 2PbO + 3O$$

Silver chromate, Ag_2CrO_4.—A dark chocolate-red precipitate, soluble in ammonia and nitric acid.

Mercurous chromate (basic), Hg_2CrO_4,Hg_2O.—A brick-red precipitate, which, when dried, and heated in a tube, gives a mercury sublimate, evolves oxygen, and leaves a residue of Cr_2O_3.

Reduction of Chromic Acid.—CrO_3 is a powerful oxidising agent, giving up oxygen to oxidisable substances, and being

itself *reduced* to Cr_2O_3 ; that is, to the condition of a " chromic " compound. Thus, by sulphur dioxide it is reduced to chromium sulphate—

$$2CrO_3 + 3SO_2 = Cr_2(SO_4)_3$$

The same action takes place in an acidified solution of potassium dichromate—

$$K_2Cr_2O_7 + H_2SO_4 + 3H_2SO_3 = Cr_2(SO_4)_3 + K_2SO_4 + 4H_2O$$
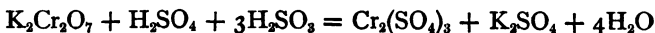
Similarly, chromic acid and chromates are reduced by HCl, oxidising the hydrogen of the acid, and liberating chlorine, after the manner of peroxides ; thus—

$$CrO_3 + 6HCl = CrCl_3 + 3H_2O + 3Cl$$
$$K_2Cr_2O_7 + 14HCl = 2CrCl_3 + 2KCl + 7H_2O + 3Cl_2$$
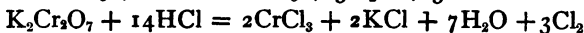
In all cases of oxidation by chromic acid, the reduction of the chromic acid compound to the state of a " chromic " compound is evidenced by the change of colour from the yellow or orange of the former, to the green colour of the latter. This reduction and change of colour is at once seen by passing sulphuretted hydrogen through acidified potassium dichromate—

$$K_2Cr_2O_7 + 3H_2S + 8HCl = 2CrCl_3 + 2KCl + 7H_2O + 3S$$
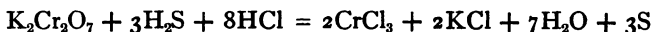
Iron, Fe

DRY REACTIONS.—Iron compounds impart to a borax bead heated in the outer flame, a colour which appears chocolate when hot, and yellow when cold. After heating in the reducing flame, the colour changes to a bottle-green (the green colour of common bottle glass is caused by the presence of iron). When heated on charcoal with Na_2CO_3 in the inner blowpipe flame, iron compounds become reduced, and a dark grey magnetic mass is obtained. If this be washed with water in a mortar, and the end of a magnet applied, it will be attracted after the manner of iron filings.

WET REACTIONS.—The salts of iron are derived from the two oxides FeO and Fe_2O_3.[1] They are both basic oxides, and give rise to two classes of salts, namely, *ferrous* and *ferric*

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[1] The oxide known as *magnetic oxide of iron*, or ferroso-ferric oxide, Fe_3O_4 or Fe_2O_3,FeO, yields a mixture of ferric and ferrous salts.

respectively. Ferrous salts readily take up oxygen, and become converted into ferric compounds; while the latter, under the influence of suitable reducing agents, easily pass back again to the ferrous condition.

(*a*) **Ferric Compounds.**—The common ferric salts that are soluble in water are the chloride, $FeCl_3$; nitrate, $Fe_2(NO_3)_6$, and sulphate, $Fe_2(SO_4)_3$. These all give yellowish-brown solutions.

NH₄HO, KHO, and NaHO throw down a brown voluminous precipitate of ferric hydroxide, $Fe_2(HO)_6$, insoluble in excess, or in NH_4Cl.[1]

K₂CO₃, Na_2CO_3, and $BaCO_3$ give the same precipitate, CO_2 being liberated—

$$2FeCl_3 + 3Na_2CO_3 + 3H_2O = Fe_2(HO)_6 + 6NaCl + 3CO_2$$
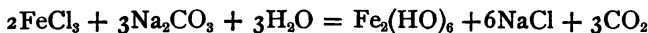
(NH₄)₂S produces a black precipitate of *ferrous* sulphide, the iron being reduced from the ferric state—

$$2FeCl_3 + 3(NH_4)_2S = 2FeS + 6NH_4Cl + S$$
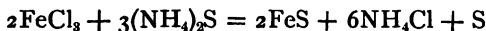
Sulphuretted hydrogen, H_2S, reduces the iron from the *ferric* to the *ferrous* state with precipitation of sulphur, but in the presence of the free acid which is developed by the action, ferrous sulphide cannot be formed. [*Ferric sulphide cannot be produced in the wet way.*]

$$2FeCl_3 + H_2S = 2FeCl_2 + 2HCl + S$$
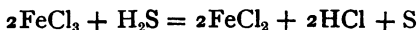
Potassium ferrocyanide, $K_4Fe(CN)_6$, or K_4FeCy_6, produces with ferric salts a dark blue precipitate (*Prussian blue*)—

$$3K_4(FeCy_6) + 4FeCl_3 = 12KCl + Fe_4(FeCy_6)_3$$
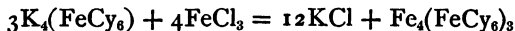
This test is extremely delicate, but where the amount of iron is very small, a blue or greenish coloration only is produced. "Prussian blue" is insoluble in hydrochloric acid, but readily dissolves in oxalic acid. It is decomposed by NaHO or KHO, with precipitation of ferric hydroxide—

$$Fe_4(FeCy_6)_3 + 12KHO = 2Fe_2(HO)_6 + 3K_4(FeCy_6)$$
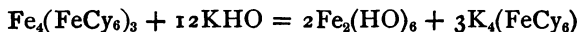
Potassium ferricyanide, $K_3(FeCy_6)$, gives no precipitate with ferric salts.

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[1] See footnote on p. 33, as to the influence of organic compounds.

Potassium thiocyanate, K(CN)S, produces with ferric salts a rich wine-red coloration, owing to the formation of ferric thiocyanate, $Fe(CNS)_3$, which is soluble in water. The colour of this compound is very intense, hence the reaction may be employed to detect very small quantities of iron.

Reduction of Ferric to Ferrous Compounds.—Fer*ric* compounds are readily reduced to the ferr*ous* state; they are therefore oxidising agents of some importance. The action of $(NH_4)_2S$ and of H_2S has been already mentioned. Nascent hydrogen reduces them in the same way; therefore, when metallic iron is dissolved in HCl or H_2SO_4, the salts produced are ferrous chloride and sulphate respectively. Nitric acid, on the other hand, converts the iron into the "ferric" state.

A ferric salt already in solution is reduced by nascent hydrogen, generated by introducing zinc into the acidified liquid.

In passing from $FeCl_3$ to $FeCl_2$, one atom of chlorine is available for oxidising purposes, and is capable of bringing about such actions as the following :—

The "oxidation". of stannous chloride, $SnCl_2$, to stannic chloride, $SnCl_4$.

The oxidation of sulphurous acid or thiosulphuric acid into sulphuric acid; thus—

$$2FeCl_3 + H_2SO_3 + H_2O = H_2SO_4 + 2HCl + 2FeCl_2$$
$$2FeCl_3 + Na_2SSO_3 + H_2O = Na_2SO_4 + 2HCl + 2FeCl_2 + S$$
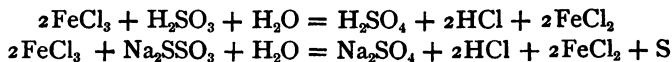
(*b*) **Ferrous Compounds.**—Ferrous salts are usually pale green when crystallised, and white when anhydrous. Of the common salts the chloride and sulphate are soluble.

NH_4HO, KHO, and NaHO produce a precipitate of ferrous hydroxide, $Fe(HO)_2$, which is at first a dirty white colour, but which rapidly turns first pale greenish-grey, then a dirty grey, and finally brown, owing to its oxidation by atmospheric oxygen. The presence of ammonium salts renders the precipitation incomplete. The precipitate is not soluble in excess of the reagents; boiling with KHO turns it black, converting it into Fe_3O_4.

K_2CO_3 and Na_2CO_3 give a white precipitate of ferrous

carbonate, $FeCO_3$, which on exposure to the air quickly absorbs oxygen.

$(NH_4)_2S$ precipitates black ferrous sulphide, FeS. Readily soluble in acids, with evolution of sulphuretted hydrogen.

$K_4(FeCy_6)$ precipitates potassium ferrous ferrocyanide, $FeK_2(FeCy_6)$, thus—

$$K_4(FeCy_6) + FeCl_2 = 2KCl + FeK_2(FeCy_6)$$
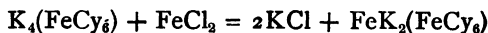
When the solutions are mixed in test-tubes in the ordinary way, the precipitate has a greenish-blue colour; but when the reaction is made in an atmosphere free from oxygen, and the solutions are previously boiled so as to entirely expel all dissolved oxygen, the precipitate is perfectly white. It rapidly absorbs oxygen and becomes blue, and is also easily oxidised to " Prussian blue " by nitric acid or chlorine; thus—

$$4FeK_2(FeCy_6) + 2Cl_2 = Fe_4(FeCy_6)_3 + K_4FeCy_6 + 4KCl$$
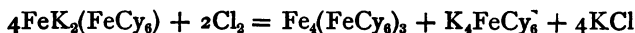
Potassium ferricyanide, $K_3(FeCy_6)$, gives with ferrous salts, a precipitate of ferrous ferricyanide, $Fe_3(FeCy_6)_2$ (known as *Turnbull's blue*), which is indistinguishable by its appearance from *Prussian* blue—

$$2K_3(FeCy_6) + 3FeCl_2 = Fe_3(FeCy_6)_2 + 6KCl$$
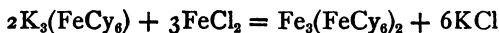
The precipitate is insoluble in hydrochloric acid, but is decomposed by caustic alkalies, with the precipitation of ferrous hydroxide; thus—

$$Fe_3(FeCy_6)_2 + 6KHO = 2K_3(FeCy_6) + 3Fe(HO)_2$$
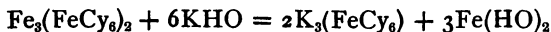
Oxidation of Ferrous to Ferric Compounds.—The ferric salts being the more stable, the ferrous compounds undergo oxidation even more readily than the ferric salts become reduced. Mere exposure to the air in many cases causes the change. In analysis the oxidation is usually accomplished either by chlorine (or bromine) or by nitric acid.

The chlorine may be employed in the form of *chlorine water*, or more conveniently by gently warming the ferrous compound with hydrochloric acid and adding a few crystals of potassium chlorate.

When the oxidation is accomplished with nitric acid, the

strong acid is added, a few drops at a time, to the hot acidulated solution of the ferrous salt. The solution becomes dark in colour, and nitric oxide is disengaged ; thus—

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 4H_2O + 2NO$$
$$3FeCl_2 + 3HCl + HNO_3 = 3FeCl_3 + 2H_2O + NO$$
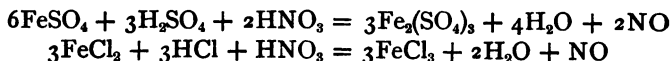
Unless the solution of the ferrous salt is acidified, a portion of the iron is converted into Fe_2O_3, which is taken up, in the case of the sulphate, by the ferric sulphate, forming insoluble basic ferric sulphates, $Fe_2(SO_4)_3, xFe_2O_3$.

Separation of Group IIIa from Groups IIIb, IV., V

To the solution add NH_4Cl in considerable quantity ; heat the mixture to boiling, and add NH_4HO carefully until precipitation is complete.[1] Bring the liquid once more "to the boil," when, if sufficient ammonia has been added, the steam will smell of it. Filter the mixture while hot. The precipitate contains the metals of Group IIIA. in the form of hydroxides, and is examined according to the table on the opposite page. The filtrate contains the metals of Groups IIIB., IV., and V.

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[1] The NH_4Cl prevents the precipitation of hydroxides of the metals of Group IIIB. and of magnesium ; it must be therefore added *plentifully*. Excess of ammonia, however, must be *avoided*, otherwise manganous hydroxide will be precipitated in spite of the ammonium chloride. (See footnote, p. 44.)

TABLE IIIA

The **precipitate** consists of $Al_2(HO)_6$, $Cr_2(HO)_6$, and $Fe_2(HO)_6$. Wash the precipitate, and transfer it (or a portion of it) to a test-tube with a small quantity of water. Add to the mixture a little sodium peroxide, and boil for a moment, until the temporary effervescence ceases. The chromium is oxidised to chromate, and the $Al_2(HO)_6$ dissolves in the NaHO, which is formed by the action of the sodium peroxide upon the water. Filter.

The **filtrate** contains sodium chromate, Na_2CrO_4, and sodium aluminate, $Al_2O_3.3Na_2O$. The former shows itself by the yellow colour. Divide into two portions—

(1) Acidify with acetic acid, and confirm **chromium** by special reactions, e.g. lead acetate.

(2) Acidify with dilute nitric acid, and add NH_4HO. A white precipitate of $Al_2(HO)_6$ confirms **aluminium**.

The **residue** consists of $Fe_2(HO)_6$. Dissolve in a little hot dilute HCl, and confirm **iron** by special reactions, e.g. K_4FeCy_6 or KCNS.[1]

[1] At this stage in the process, the iron will be in the "ferric" condition. To ascertain whether it was originally present as a "ferrous" or "ferric" compound, separate tests must be made in the solution *before* it has been subjected to the action of either reducing or oxidising agents.

The following alternative methods of separation may also be used :—

(*a*) The precipitated hydroxides are washed and dried. The residue is then mixed with at least six times its weight of *fusion mixture*,[1] and fused in a platinum capsule. In this way the chromium is converted into alkaline chromate ; a variable proportion of the aluminium into aluminates.

The fused mass is then dissolved in water, and filtered. The filtrate is tested for aluminium and chromium, while the residue is dissolved and tested for iron, as in the foregoing scheme.

(*b*) The precipitated hydroxides are dissolved in a little warm dilute HCl, and pure NaHO[2] added in quantity considerably more than sufficient to produce precipitation. The mixture is then boiled for a few minutes, and filtered.

The filtrate contains sodium aluminate, $Al_2O_3,3Na_2O$. Add dilute HCl until just acid, and reprecipitate $Al_2(HO)_6$ with ammonia.

The precipitate contains $Cr_2(HO)_6$ and $Fe_2(HO)_6$. This is dried, and fused with fusion mixture. The fused mass is dissolved in water and filtered. The solution contains sodium chromate, while the Fe_2O_3 remains on the filter. These are confirmed as in the above methods.

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[1] *Fusion mixture* is a mixture of Na_2CO_3 and K_2CO_3 in equivalent proportions (or about 10 parts Na_2CO_3 to 13 of K_2CO_3). It is used in preference to Na_2CO_3 alone, because it has the property of melting more easily than either carbonate separately.

[2] The commercial caustic soda usually employed in the laboratory always contains more or less sodium aluminate. The student should test a sample of the reagent by neutralising it with HCl, and then adding NH_4HO. In the method of separation given in Table IIIA., this difficulty is avoided, as the sodium peroxide of commerce is usually free from this impurity.

Manganese, Mn

DRY REACTIONS.—Manganese compounds, when heated in a borax bead in the oxidising flame, impart to the bead a violet or lilac colour. When heated in the reducing flame, the bead again becomes colourless.

A more characteristic reaction is to fuse the manganese compound with KHO, or with Na_2CO_3 and a little KNO_3 or $KClO_3$ upon a piece of platinum foil; the manganese undergoes oxidation, and a deep green-coloured mass is obtained, consisting of manganates of the alkali metals—

$$MnO_2+Na_2CO_3+O \text{ (from } KClO_3 \text{ or } KNO_3)=Na_2MnO_4+CO_2$$

WET REACTIONS.—Of the common manganous [1] salts, the chloride, $MnCl_2,4H_2O$, and the sulphate, $MnSO_4,5H_2O$, are soluble in water. In the crystallised state they have all a pink colour. Manganous salts which are soluble in water do not undergo atmospheric oxidation.

NH_4HO, KHO, and NaHO produce a white precipitate of manganous hydroxide, $Mn(HO)_2$. Insoluble in excess of the reagent, the precipitate quickly absorbs oxygen, and is converted into hydrated manganic oxide, Mn_2O_3,H_2O, having a brown colour.

Freshly precipitated $Mn(HO)_2$, while still white, is soluble in NH_4Cl; therefore in the presence of NH_4Cl, manganous hydroxide is not precipitated by NH_4HO, and only incompletely by KHO or NaHO.

The ammoniacal solution of the double chloride, however, is capable of absorbing oxygen just as the precipitated $Mn(HO_2)$

[1] The mangan*ic* salts are extremely unstable in solution, and do not exist under the ordinary conditions of analysis.

does, and the liquid quickly becomes muddy, owing to the precipitation from it of the brown hydrated manganic oxide.[1]

$(NH_4)_2S$ precipitates manganous sulphide, MnS, as a pale pinkish-white compound, easily soluble in dilute acids (*distinction from* Ni *and* Co), soluble also in acetic acid (*distinction from* Zn). Precipitation with $(NH_4)_2S$ is only complete in the presence of NH_4Cl. Owing to the ready solubility of MnS in acids, H_2S is incapable of precipitating manganous sulphide from neutral solutions; for, by double decomposition, the acid of the manganous salt would be set free, and would immediately redissolve the sulphide.

Manganese Compounds as Oxidising Agents.—When manganese dioxide is acted upon by acids, a manganous salt is formed, and available oxygen is eliminated, which either appears as free oxygen gas, or as the product of the oxidation of the acid; thus—

$$MnO_2 + H_2SO_4 = MnSO_4 + H_2O + O$$
$$MnO_2 + 4HCl = MnCl_2 + 2H_2O + Cl_2$$

The manganates and permanganates are still more powerful oxidizing agents, the former containing 2 and the latter $2\frac{1}{2}$ atoms of available oxygen in the molecule—

$$K_2MnO_4 = K_2O,MnO,O_2$$
$$2KMnO_4 = K_2O,2MnO,5O$$

Or, when acted upon by hydrochloric acid the equivalent quantity of chlorine is evolved—

$$KMnO_4 + 8HCl = KCl + MnCl_2 + 4H_2O + 5Cl$$
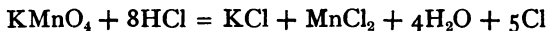
Potassium permanganate in acid solution is therefore capable of oxidising a great variety of oxidisable compounds, giving up its available oxygen, and becoming itself reduced to a

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[1] For this reason the complete separation of manganese from the metals of Group IIIA. is difficult to accomplish. If care be taken to ensure the presence of sufficient NH_4Cl, and if the precipitation with NH_4HO be made as quickly as possible with the least possible excess of ammonia in a hot solution, and the excess of ammonia at once boiled off, and the liquid filtered immediately, the risk of precipitating the manganese may be reduced to a minimum. The student will do well to practise the separation of manganese from the metals of Group IIIA. by using solutions containing known small proportions of a manganous salt, mixed with large quantities of iron or chromium or aluminium.

manganous salt, the characteristic purplish colour of the permanganate of course being destroyed. The reaction with ferrous sulphate may be taken as a typical example. Two molecules of this salt in presence of sulphuric acid require one atom of oxygen for their oxidisation—

$$2FeSO_4 + H_2SO_4 + O = H_2O + Fe_2(SO_4)_3$$

Hence one molecule of $KMnO_4$ is capable of oxidising five molecules of $FeSO_4$; or, in the presence of HCl, of oxidising five molecules of $FeCl_2$ into $FeCl_3$.

Zinc, Zn

DRY REACTIONS.—Zinc compounds give no characteristic borax bead.

When heated on charcoal with sodium carbonate in the reducing flame, zinc compounds are reduced, but the metal is too volatile to appear in the form of globules. As it is reduced, it volatilises; and the vapour burns as it passes through the outer flame, which thereby becomes tinged a bluish-white colour. The zinc oxide which is thus produced, deposits as an incrustation upon the charcoal, which is canary-yellow while hot, becoming white on cooling. Zinc oxide is not volatile, and therefore the incrustation does not disappear when the oxidising flame is made to play upon it. If the zinc oxide be moistened with a drop of cobalt nitrate, and again heated in the oxidising flame, it assumes a green colour.

WET REACTIONS.—Of the common salts the chloride, sulphate, and nitrate are soluble in water.

NaHO, or KHO, throws down a white precipitate of $Zn(HO)_2$, readily soluble in excess of the reagent, forming double salts (sometimes called *zincates*), such as $ZnNa_2O_2$. Moderately strong solutions of these zincates may be boiled without undergoing any change, but from dilute solutions $Zn(HO)_2$ is reprecipitated. NH_4HO precipitates the same compound, also soluble in excess of ammonia. $Zn(HO)_2$ is soluble in NH_4Cl, owing to its readiness to form soluble double salts with the alkaline chlorides, having the general formula $ZnCl_2, 2RCl$—

$$Zn(HO)_2 + 4NH_4Cl = ZnCl_2, 2NH_4Cl + 2NH_4HO$$

Hence in the presence of much ammonium chloride, NH_4HO gives no precipitate, and the precipitation with KHO or NaHO is incomplete.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ produces a white precipitate of basic carbonate; the precipitate is soluble in excess of $(NH_4)_2CO_3$. The presence of much NH_4Cl prevents the precipitation.

$(NH_4)_2S$ throws down a white precipitate of zinc sulphide, ZnS. In the presence of NH_4Cl the precipitation is complete even from dilute solutions. ZnS is soluble in dilute mineral acids, hence H_2S is incapable of completely precipitating this sulphide from neutral solutions of the zinc salts of such acids—

$$ZnCl_2 + H_2S \rightleftarrows ZnS + 2HCl$$

ZnS is insoluble in acetic acid (contrast MnS), therefore from the acetate, *or other zinc salts in presence of an alkaline acetate*, ZnS is completely precipitated by H_2S; thus—

$$Zn(C_2H_3O_2)_2 + H_2S = ZnS + 2H(C_2H_3O_2)$$
$$ZnCl_2 + 2Na(C_2H_3O_2) + H_2S = ZnS + 2NaCl + 2H(C_2H_3O_2)$$
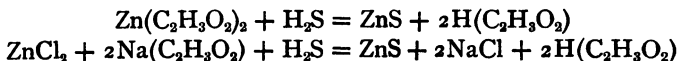
Nickel, Ni

DRY REACTIONS.—Nickel compounds impart a dark red-brown colour to the borax bead when heated in the oxidising flame, the colour becoming brownish-yellow on cooling. In the reducing flame the borax bead becomes opaque and grey. In a bead of microcosmic salt, the red-brown colour persists in both flames.

The presence of other colour-producing oxides renders this test uncertain, while even traces of cobalt entirely mask it. Heated on charcoal with Na_2CO_3, metallic nickel is obtained as a grey feebly magnetic mass.

WET REACTIONS.—Only one of the oxides of nickel is basic, namely NiO, hence only one series of salts exists. The sesquioxide, Ni_2O_3, behaves like a peroxide; thus—

$$Ni_2O_3 + 2H_2SO_4 = 2NiSO_4 + 2H_2O + O$$
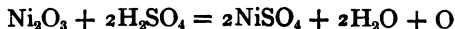
In the crystalline or hydrated condition the nickel salts have a

green colour, and dissolve to green solutions. The anhydrous salts are pale yellow. Of the common salts, the chloride, nitrate, and sulphate are soluble in water.

KHO or NaHO gives a pale bluish-green precipitate of nickelous hydroxide, $Ni(HO)_2$, insoluble in excess of either reagent; soluble in ammonium salts. $Ni(HO)_2$ is not oxidised on exposure to air, but it is converted into black hydrated sesquioxide, $Ni_2O_3,3H_2O$, by hypochlorites, or by the action of chlorine or bromine in the presence of caustic alkalies; thus—

$$2Ni(HO)_2 + NaClO + H_2O = NaCl + Ni_2O_3,3H_2O$$
$$2Ni(HO)_2 + 2NaHO + Cl_2 = 2NaCl + Ni_2O_3,3H_2O$$
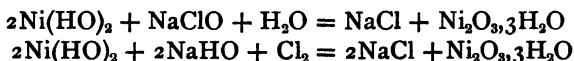
NH₄HO gives a greenish precipitate in neutral solutions of a basic compound, readily soluble in excess of ammonia to a greenish-blue solution. In the presence of ammonium salts, no precipitate is produced by ammonia. The nickel in this solution is not oxidised by hypochlorites, but it is completely precipitated, as $Ni(HO)_2$, on the addition of KHO.

K₂CO₃, Na_2CO_3, or $(NH_4)CO_3$ produces a pale-green precipitate of basic carbonate, $xNiCO_3,yNi(HO)_2$, soluble in excess of ammonia to a bluish solution.

(NH₄)₂S, or H_2S in presence of ammonia, produces a black precipitate of NiS, soluble to a slight extent in excess; more readily soluble if ammonia or polysulphides of ammonia are present, yielding a brown solution. From this solution the dissolved NiS is reprecipitated slowly on boiling, more quickly after acidifying with acetic acid, or the addition of ammonium acetate.

NiS is only difficultly soluble in strong HCl, and almost insoluble in the dilute acid; also in acetic acid. Readily soluble in *aqua regia*, or in HCl and a crystal of $KClO_3$, yielding $NiCl_2$; soluble also in HNO_3.

H_2S only produces *complete* precipitation of NiS from a warm solution of the acetate, or from other nickel salts in the presence of an alkaline acetate. In the case of neutral solutions of nickel salts with mineral acids, the precipitation is only partial, while in acid solutions it does not take place at all.

KCy gives a pale-green precipitate of nickelous cyanide,

NiCy$_2$, readily soluble in excess of the reagent forming the double cyanide, K$_2$NiCy$_4$. From this solution (NH$_4$)$_2$S fails to precipitate the sulphide. Dilute mineral acids cause the reprecipitation of nickelous cyanide—

$$K_2NiCy_4 + 2HCl = 2KCl + 2HCy + NiCy_2$$

Boiling with hydrochloric acid decomposes the metallic cyanide altogether—

$$K_2NiCy_4 + 4HCl = 2KCl + 4HCy + NiCl_2$$

Oxidising agents, such as hypochlorites, chlorine, or bromine precipitate the black hydrated sesquioxide. (*Distinction from cobalt.*)

$$2K_2NiCy_4 + NaClO + 5H_2O = Ni_2O_3,3H_2O + NaCl$$
$$+ 4KCy + 4HCy$$
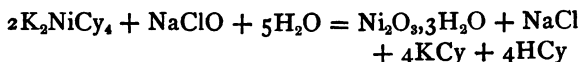
Cobalt, Co

DRY REACTIONS.—Cobalt compounds impart to a borax bead a rich blue colour, when heated either in the oxidising or reducing flame. The test is characteristic and delicate.

WET REACTIONS.—Cobalt forms a number of oxides, two only of which are basic. The *cobaltous salts* are derived from CoO, while the feebly basic sesquioxide Co$_2$O$_3$ forms the very unstable cobaltic salts.

Of the common cobaltous salts, the sulphate, nitrate, and haloid salts are soluble in water. In the hydrated condition they have a pink colour, dissolving to pink solutions. In the anhydrous state they are blue. A strong aqueous solution (pink) will, however, turn blue when boiled, and return to its original pink colour when again cooled.

KHO or NaHO gives a greenish-blue precipitate of a basic salt. On boiling with excess of the alkali, the precipitate is converted into the pink hydroxide, Co(HO)$_2$, which, however is coloured more or less brown by the oxidation of a portion, of it (by atmospheric oxygen) into the hydrated cobaltic oxide, Co$_2$O$_3$,3H$_2$O, or Co$_2$(HO)$_6$.

Co(HO)$_2$ is oxidised by hypochlorites, in the same manner as the corresponding nickel compound.

NH₄HO causes partial precipitation of a basic salt, which dissolves easily in excess of ammonia or in ammoniacal salts. The solution, which has a brownish colour, absorbs oxygen, and becomes darker in colour.

K₂CO₃, Na₂CO₃, or (NH₄)₂CO₃ precipitates a lilac-coloured basic carbonate, $xCoCO_3$, $yCo(HO)_2$, readily soluble in excess of (NH₄)₂CO₃ to a reddish solution.

HKCO₃ gives a pinkish precipitate of normal cobalt carbonate, CoCO₃. The precipitate so obtained is soluble in hydrogen peroxide, yielding a deep *green* solution.

(NH₄)₂S gives a black precipitate of cobaltous sulphide, CoS. The precipitation is complete in the presence of NH₄Cl (contrast NiS). CoS is soluble in HNO₃, in "aqua regia," and in HCl with the addition of a crystal of KClO₃; difficultly soluble in strong HCl; practically insoluble in dilute HCl.

H₂S precipitates CoS under the same conditions as apply in the case of NiS.

KCy gives a reddish precipitate of CoCy₂ soluble in excess of the reagent, forming potassium cobaltocyanide, K₄CoCy₆ (corresponding to potassium ferrocyanide) (*contrast nickel*). The addition of oxidising agents—hypochlorites, chlorine, or bromine—to this solution produces no precipitation of cobalt sesquioxide, but oxidises the *cobaltocyanide* into *cobalticyanide*. (*Distinction from nickel.*)

$$2K_4CoCy_6 + NaClO + H_2O = NaCl + 2KHO + 2K_3CoCy_6$$
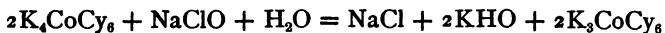
SEPARATION OF GROUP IIIB. FROM GROUPS IV. AND V

Add NH₄Cl, NH₄HO,[2] and pass H₂S through the solution (or add (NH₄)₂S, drop by drop, avoiding excess; see Nickel) until precipitation is complete. Warm gently, and filter.

---

[1] Solutions of these double cyanides do not give precipitates with the reagents usually employed for the detection of the metals, because on dissociation they do not yield ions of the metal, but complex ions of the metal and cyanogen. For example, such cyanides as K₂NiCy₄ yield $2\overset{+}{K} + \overset{-}{NiCy_4}$, while compounds such as the ferrocyanides and cobaltocyanides yield the ions $\overset{-}{FeCy_6}$ and $\overset{-}{CoCy_6}$ respectively.

[2] In the ordinary course of analysis, these reagents have already been added for the separation of Group IIIA.

TABLE IIIb

Separation of the Metals of Group IIIb

The **precipitate**, consisting of MnS, ZnS, NiS, and CoS, is dissolved in hot dilute HCl, with the aid of a few particles of KClO₃.[1] The solution is boiled until it no longer smells of chlorine, and NaHO added in excess. It is again boiled (to ensure the solution of all the Zn(HO)₂), and filtered after cooling (hot NaHO will attack the filter-paper).

The **solution** contains sodium zincate, ZnNa₂O₂. Pass H₂S through the liquid (or add H₂S water), when a white precipitate of ZnS is produced.	The **precipitate**, consisting of Mn(HO)₂, Ni(HO)₂, and Co(HO)₂, is washed to remove the soluble zinc salt still adhering to it, and then dissolved in the smallest quantity of warm HCl. The solution is *nearly* neutralised with NH₄HO, a considerable quantity of ammonium acetate added, and H₂S passed through the mixture until precipitation is complete.	
	The **solution** contains manganous acetate, Mn(C₂H₃O₂)₂. Precipitate MnCO₃ by adding Na₂CO₃. Filter; wash thoroughly; dissolve in HCl, and confirm Mn by precipitation of the pinkish MnS, with (NH₄)₂S after NH₄Cl and NH₄HO. The formation of the green manganate may also be used as a confirmatory test.	The **precipitate** (NiS and CoS). Test a small portion with a borax bead. Blue colour indicates cobalt. Dissolve the precipitate in the least quantity of *aqua regia*; boil off the excess of acid, and nearly neutralise with Na₂CO₃ (avoid dilution). Add KCy (freshly made solution) until the precipitated cyanides are *just* redissolved, add NaHO in considerable quantity, and then bromine water[2] until the colour of the bromine persists. Filter.
		The **solution** contains sodium cobalticyanide, Na₃CoCy₆. The cobalt may be confirmed by the borax bead, if the test was not made, or was not satisfactory, with the sulphides.	The **precipitate** consists of the black hydrated sesquioxide of nickel, Ni₂O₃3H₂O. Confirm (1) by borax bead; (2) wash precipitate, dissolve in HCl, and obtain the characteristic reaction with (NH₄)₂S.

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[1] Should the precipitate not be black, only MnS and ZnS can be present; and as these are easily soluble in HCl, the KClO₃ should in this case not be added.

[2] Bromine is more soluble in water containing KBr in solution than in water alone. By the use of such a solution, therefore, unnecessary dilution is avoided.

SEPARATION OF PHOSPHORIC ACID.

As stated on p. 20, there are conditions under which the group reagent for Group IIIA. fails to separate the metals of this group from those which follow. The presence of phosphates is such a condition. The phosphates of all the metals of Groups III. and IV., as well as of magnesium, are soluble in hydrochloric acid, and are reprecipitated on the addition of ammonia. Hence the precipitate obtained by ammonia, in the process of separating Group IIIA., *may* contain any or all of these phosphates, in addition to the hydroxides of iron, chromium, and aluminium. Before proceeding to the separation of Groups IIIA. and IIIB., therefore, it is essential first to ascertain whether or not any phosphates are present; and second, if they are found present, to adopt measures to remove the phosphoric acid.

Test for Phosphoric Acid.—To a small quantity of the solution add a large excess (four or five times the volume) of a nitric-acid solution of ammonium molybdate $(NH_4)_2MoO_4$, and gently warm the mixture, when a bright yellow precipitate of ammonium phospho-molybdate separates out.[1]

The removal of Phosphoric Acid is based upon the fact that ferric phosphate (also the phosphates of Al and Cr) is insoluble in acetic acid. Thus, if acetic acid or sodium acetate (in practice, a mixture of the two is employed) be added to a hydrochloric acid solution of ferric phosphate, and the mixture boiled, the ferric phosphate is precipitated; also, if ferric chloride is added to an acid solution of any of the phosphates soluble in that acid (*i.e.* the phosphates of metals of Groups IIIB., IV., and magnesium), by double decomposition ferric phosphate is thrown down, and chlorides of the other metals are left in solution. For example—

$$Ca_3(PO_4)_2 + 2FeCl_3 \text{ (in presence of acetic acid)} = Fe_2(PO_4)_2 + 3CaCl_2$$
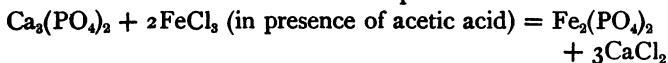
The process is carried out according to the scheme given in Table IIIc. on the following page.

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[1] Arsenic acid gives a similar yellow precipitate of ammonium arseno-molybdate; therefore the test for phosphoric acid must not be applied until arsenic has been removed in Group II.

The precipitate produced by NH_4HO in presence of NH_4Cl may consist of Groups III. and IV., and of Mg. Dissolve in a little dilute HCl, and acetic acid [1] (reagent).

The **Precipitate** may consist of phosphates of Fe, Al, Cr (along with basic acetate of iron). This precipitate may be treated with Na_2O_2 exactly as the hydroxides (Table IIIA., p. 41) $Al_2(PO_4)_2$ dissolves, the $Cr_2(PO_4)_2$ is oxidised to Na_2CrO_4. On filtering, the iron remains on the filter. Aluminium is detected by neutralising and reprecipitating with ammonia; the chromium by barium chloride in acetic acid solution.	The **Filtrate**. To a small portion If a precipitate is produced, drop, until the whole of the the precipitation is seen by the mixture,[3] and filter. If the preliminary test with ferric contains no more phosphoric <hr>The **Precipitate** consists of ferric phosphate and basic acetate. ——— Throw away.

[1] If the addition of sodium acetate gives no precipitate, it follows analysis (see previous page).

If, after the addition of the acetate reagent, and before the mixture allowing the precipitate to settle somewhat), this means that ferric acetate solution); and if this is formed, it follows that there is present in the present; hence all the phosphoric acid will have passed into the precipitate excess of ferric chloride upon the sodium acetate. Thus—

[2] Boiling the mixture at this point ensures the conversion of the soluble solution should be colourless, or entirely free from the *red* colour.

[3] The boiling here is for the same reason as that in the foregoing note. precipitated ferric phosphate is soluble in ferric chloride and in ferric

of hydroxides of Al, Fe, Cr, as well as phosphates of any of the metals avoiding excess. Nearly neutralise with Na_2CO_2, and add sodium acetate Boil the mixture,[2] and filter.

---

of the liquid, which should be colourless, add a drop of ferric chloride. then ferric chloride is added to the main portion of the filtrate, drop by phosphoric acid is thrown down as ferric phosphate. The completion of liquid becoming *red*, by the formation of ferric acetate. Boil the

chloride gave no precipitate, but only a red coloration, then the solution acid, and is at once treated as in the next step.

The **Solution.** Add NH_4Cl, heat to boiling, and add NH_4HO.
Filter.

The **Precipitate** may consist of $Al_2(HO)_6$ and $Cr_2(HO)_6$. ——— Examine in usual way. Table IIIA.	The **Filtrate.** Examine for Groups IIIB. and IV., and for magnesium in the usual way. Tables IIIB., IV., and V.

that no iron, aluminium, or chromium are present in the substance under

has been boiled, the liquid itself appears *red* (which is easily seen by is being produced (which is soluble in sodium acetate, forming a red mixture *more than enough iron* to unite with *all the phosphoric acid* along with the iron. This ferric acetate is formed by the action of the

$$FeCl_2 + 3Na(C_2H_3O_2) = Fe(C_2H_3O_2)_3 + 3NaCl$$
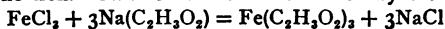
ferric acetate into the insoluble basic acetate, so that when filtered the

It is important to avoid any unnecessary excess of $FeCl_3$, because the acetate.

CHAPTER VII

REACTIONS OF THE METALS OF GROUP II

THIS group is conveniently divided into two sections—

Subdivision 1. Mercury, lead, bismuth, cadmium, copper.
Subdivision 2. Arsenic, antimony, tin.

SUBDIVISION 1

Mercury, Hg

DRY REACTIONS.—When heated alone in a tube, many mercury compounds (those with the halogens, for example) volatilise unchanged, giving sublimates of the same compound. The iodide (red) when heated forms a sublimate, consisting chiefly of the yellow allotropic form of HgI_2, which when cold changes to red if scratched or rubbed. Some mercury compounds, *e.g.* the oxide, yield a sublimate of metallic mercury.

If a mercury salt be mixed with several times its weight of sodium carbonate (both being as dry as possible), and the mixture be strongly heated in a dry narrow test-tube, a sublimate of metallic mercury will be obtained. The sublimed mercury will present the appearance of a bright metallic mirror, but if examined by means of a lens, or if rubbed with a glass rod, distinct globules of liquid metal will be visible.

WET REACTIONS.—Mercury forms two classes of salts, namely, the mercu*ric* and the mercu*rous* salts. The former compounds contain the divalent atom or radical Hg″, while the mercurous salts contain the divalent double atom or radical $(Hg_2)''$.

The metal in its mercu*ric* compounds belongs to Group II.,

54

while in its mercu*rous* salts it falls in Group I.   For conveni-
ence the reactions of both the $\overset{+}{\text{Hg}}$ ion and the $(\overset{+}{\text{Hg}_2})$ ion will
be studied in this place.

(*a*) **Mercuric Compounds.**—Of the common salts, the nitrate,
sulphate, chloride, and bromide (*but not the iodide*) are soluble
in water, but the solubility is not very great.

KHO or NaHO gives with mercuric compounds a yellow
precipitate [1] of mercuric oxide, HgO—

$$HgCl_2 + 2KHO = HgO + H_2O + 2KCl$$

The precipitate is insoluble in excess of the reagent.

NH₄HO produces a white precipitate of an ammoniacal
mercuric compound, where two atoms of hydrogen from the
ammonium radical are replaced by the divalent atom Hg;
thus—

$$HgCl_2 + 2NH_4HO = NH_2HgCl + NH_4Cl + 2H_2O$$

H₂S produces a black precipitate of HgS.   At first the
precipitate is white, changing rapidly through yellow and
brown to black.   The white compound consists of $HgCl_2$,
$2HgS$ (or $Hg(NO_3)_2$, $2HgS$ when the nitrate is used).   These
colour changes are characteristic.   The precipitation is only
complete after some time, and when the solution is consider-
ably dilute.   The compound is insoluble in HCl, and in
HNO_3 even when boiling.   (The prolonged action of boiling
HNO_3 partially converts it into the white compound $Hg(NO_3)_2$,
$2HgS$.)   Mercuric sulphide dissolves in *aqua regia*, forming
mercuric chloride.   In the presence of caustic alkalies it dis-
solves in sodium or potassium sulphide (*not in ammonium
sulphide*), forming the double sulphides, HgS,Na₂S and
HgS,K₂S.

KI precipitates HgI₂ as a rich scarlet compound, soluble

---

[1] On the first addition of the reagent, the precipitate appears a brownish
colour (probably due to the momentary formation of the hydroxide, which
is incapable of existing), but almost immediately it becomes yellow.   Why
the oxide obtained by precipitation should be yellow, while that prepared
in the dry way is brick-red, is not known.   Compare also the sulphide.

in excess of either solution. When first precipitated it appears yellow, but quickly turns salmon-red, and then scarlet.

Reduction of Mercuric Compounds.—By reducing agents mercuric compounds may be converted into mercurous salts, or the reduction may go a stage further and result in the precipitation of mercury. Thus, on the addition of stannous chloride, $SnCl_2$, a white precipitate of mercurous chloride is produced—

$$2HgCl_2 + SnCl_2 = Hg_2Cl_2 + SnCl_4$$
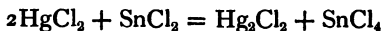
On gently warming with an excess of stannous chloride, the precipitated mercurous chloride changes to a grey deposit of mercury in a condition of fine powder—

$$Hg_2Cl_2 + SnCl_2 = SnCl_4 + 2Hg$$
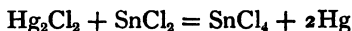
Many metals are capable of displacing mercury from its solutions, the mercury being deposited upon the metal. Thus, if a strip of clean copper be immersed in a neutral or slightly acid solution of a mercury salt, it becomes coated with a greyish deposit, from which the mercury can be readily volatilised and obtained as a metallic sublimate by heating the copper in a dry test-tube.

(*b*) **Mercurous Compounds.**—Of the common salts mercurous nitrate is the only one which is readily soluble, and this only so long as the water is acid with nitric acid. The addition of much water results in the precipitation of a basic nitrate. Mercurous sulphate is soluble with difficulty.

KHO or NaHO throws down a black precipitate of $(Hg_2)O$. Mercurous oxide is very unstable. When gently warmed, or even upon exposure to light, it is converted into HgO and Hg.

NH$_4$HO precipitates an ammoniacal mercurous compound, which is black.

$$Hg_2(NO_3)_2 + 2NH_4HO = NH_2(Hg_2)NO_3 + NH_4NO_3$$
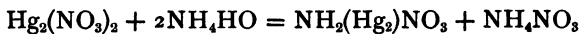
H$_2$S produces a black precipitate, which is a mixture of HgS and Hg. This precipitate, therefore, behaves, on treatment with nitric acid, in the same way as that obtained from a *mercuric* solution, giving the white insoluble compound $Hg(NO_3)_2,2HgS$.

HCl and soluble chlorides precipitate white mercurous chloride, Hg_2Cl_2. Insoluble in dilute acids; soluble in boiling HNO_3, being converted into $HgCl_2$ and Hg, and the mercury then dissolves to mercuric nitrate, with evolution of oxides of nitrogen.

Ammonia converts it into *black* mercurous ammonium chloride, $NH_2(Hg_2)Cl$. (This constitutes one of the most characteristic reactions for mercurous compounds.)

Mercurous salts are reduced to metallic mercury by the reducing agents which reduce the mercuric compounds; thus, with stannous chloride a grey precipitate of mercury is at once produced—

$$Hg_2(NO_3)_2 + SnCl_2 + 2HCl = SnCl_4 = 2HNO_3 + 2Hg$$
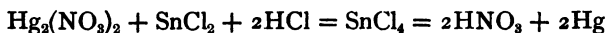
Lead, Pb

DRY REACTIONS.—Lead compounds are very readily reduced when heated upon charcoal before the blowpipe flame, either alone or mixed with sodium carbonate or potassium cyanide. Globules of metallic lead are thus obtained, and at the same time a yellowish incrustation is formed, consisting of the oxide PbO (*litharge*). When cold, one of the globules can be removed and the properties of the metal examined. Lead may be recognised by its malleability and softness, the latter property enabling it to leave a black mark when rubbed upon paper.

WET REACTIONS.—The only salts of lead which are met with in analysis are derived from plumbic oxide, PbO, in which the metal is divalent. Of the common salts, the nitrate and acetate are readily soluble in water; the chloride, bromide, and iodide are sparingly soluble.

KHO, NaHO, or NH_4HO gives a white precipitate of lead hydroxide, $Pb(HO)_2$ (usually admixed with a basic compound), soluble in excess of KHO or NaHO, but not in NH_4HO.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ gives a precipitate of basic carbonate of lead.

H_2S gives a black precipitate of lead sulphide, PbS. In

the presence of much hydrochloric acid, the precipitate first formed consists of a brown compound having the composition $PbCl_2, 2PbS$, which by the further action of H_2S is converted into the black PbS.

PbS is insoluble in cold dilute acids, in alkalies, or in the sulphides of the alkalies. It is readily dissolved by hot dilute HNO_3, giving lead nitrate and free sulphur. As the strength of the acid is increased, this sulphur begins to be oxidised into sulphuric acid, which causes the precipitation of lead sulphate.

Strong nitric acid converts lead sulphide entirely into the sulphate.

H_2SO_4 and soluble sulphates give a white precipitate of lead sulphate, $PbSO_4$. Very slightly soluble in water; less soluble in the presence of either dilute sulphuric acid or alcohol; hence, in very dilute solutions, precipitation is accelerated by the addition of alcohol. $PbSO_4$ dissolves by long boiling with strong HCl, yielding $PbCl_2$. It dissolves more readily in strong ammoniacal solutions of ammonium acetate or tartrate, as well as in hot KHO or NaHO. From these it is again precipitated on addition of H_2SO_4.

HCl and soluble chlorides give a white precipitate of lead chloride, $PbCl_2$. The precipitate is slightly soluble in cold water, moderately freely in boiling water; from which solution it separates on cooling in long white needle-shaped crystals. The presence of free HCl diminishes its solubility in cold water. Owing to this partial solubility of the chloride, lead is not completely separated by the group-reagent for Group I., and therefore is met with also among the metals of Group II.

KI gives a yellow precipitate of PbI_2. Soluble, but to a less extent than the chloride, in boiling water to a colourless solution.

K_2CrO_4 precipitates yellow lead chromate, $PbCrO_4$, insoluble in acetic acid. Soluble in dilute HNO_3 and in caustic alkalies (see reactions for chromium).

Bismuth, Bi

DRY REACTIONS.—Bismuth compounds are easily reduced when heated with Na_2CO_3 upon charcoal. The metal, however,

rapidly oxidises when strongly heated, hence the charcoal becomes covered with an incrustation of the pale yellow oxide, Bi_2O_3, the colour of which (as is the case with most coloured oxides) appears darker (orange-yellow) while hot. Globules of the metal, if detached from the charcoal, may be at once distinguished from lead or silver by their brittleness. Bismuth dissolves easily in HNO_3, but is scarcely attacked by HCl, or by dilute H_2SO_4.

WET REACTIONS.—Of the common salts of bismuth none are soluble in water in the ordinary sense, but the nitrate and chloride are readily soluble in water acidified with the respective acids. Water alone, converts these salts into basic compounds, which are soluble in acid; the action, therefore, is reversible—

$$Bi(NO_3)_3 + 2H_2O \rightleftarrows Bi(HO)_2NO_3 + 2HNO_3$$

In the case of bismuth chloride, the oxychloride is thrown down—

$$BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl$$
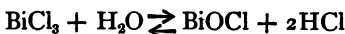
This compound is not so easily dissolved by HCl as the basic nitrate is by HNO_3, therefore the whole of the bismuth will be precipitated if the solution is dilute.

The precipitate is not dissolved by tartaric acid. (*Distinction from antimony.*)

KHO or NaHO precipitates the white hydroxide $Bi(HO)_3$, or $Bi_2O_3,3H_2O$. Insoluble in excess of the precipitants. From boiling solutions, or on heating to boiling, the basic compound is formed, BiO(HO) or Bi_2O_3,H_2O.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ throws down a white basic carbonate, $(BiO)_2CO_3$. Insoluble in excess of the reagents.

H_2S or $(NH_4)_2S$ precipitates bismuthous sulphide, Bi_2S_3, as a dark brown, almost black, compound. Soluble in HNO_3; insoluble in alkaline sulphides.

$K_2Cr_2O_7$ precipitates basic bismuth dichromate, $(BiO)_2Cr_2O_7$. *Insoluble in* KHO. (*Distinction from lead.*)

Cadmium, Cd

DRY REACTIONS.—Cadmium compounds, heated on charcoal with sodium carbonate, are easily reduced; but, owing to the ready volatility of the metal, the latter is converted into the oxide, which is deposited as a brown incrustation upon the charcoal.

WET REACTIONS.—Of the common salts, the nitrate, sulphate, chloride (bromide, iodide, and acetate) are soluble in water.

KHO, NaHO, or NH_4HO precipitates the white hydroxide, $Cd(HO)_2$. Insoluble in excess of KHO or NaHO, but soluble in NH_4HO.

K_2CO_3, Na_2CO_3, or $(NH_4)_2CO_3$ gives a white precipitate of $CdCO_3$. The presence of NH_4HO prevents the precipitation.

H_2S or $(NH_4)_2S$ precipitates cadmium sulphide, CdS, distinguished from the sulphides of all the other metals of this division by its pure yellow colour. It is more easily soluble in acids than the other sulphides of the group, and therefore, to ensure complete precipitation, the solution must not be too strongly acid.

CdS is insoluble in potassium cyanide, and is precipitated by H_2S from a solution of $CdCy_2$ in excess of KCy (see Method of Separation from Copper). CdS is insoluble in alkaline sulphides, which distinguishes it from arsenious sulphide, which is the only other yellow sulphide (see p. 55).

Copper, Cu

DRY REACTIONS.—Copper compounds are reduced to metallic copper when strongly heated upon charcoal along with sodium carbonate in the reducing flame. Reddish scales, or even globules, of metal will be found. Heated in a borax bead, copper salts impart a colour which is green while the bead is hot, but bluish when cold. Heated on a platinum wire they give a green flame, which appears bright blue if the substance is moistened with strong HCl and reintroduced into the flame.

WET REACTIONS.— Copper forms two series of salts, *cuprous*

and *cupric*, derived from the two oxides Cu_2O and CuO. The former readily pass by oxidation into cupric compounds.

(*a*) **Cupric Salts.**—Of the common *cupric* salts, the sulphate, nitrate, chloride (bromide and acetate) are readily soluble in water. In the crystallised or hydrated condition they are blue or green, but in the anhydrous state either white or pale yellow.

KHO or **NaHO** produces a pale blue precipitate of cupric hydroxide $Cu(HO)_2$. Insoluble in excess. On boiling the mixture, the hydroxide is converted into black cupric oxide.

NH_4HO or **$(NH_4)_2CO_3$** precipitates a light blue basic compound, readily soluble in excess to a deep blue solution (characteristic of copper compounds).

K_2CO_3 or **Na_2CO_3** gives a greenish precipitate of the basic carbonate, $Cu(CO_3),Cu(HO)_2$. Insoluble in excess of the reagent.

KCy gives with *both cupric and cuprous* salts a white precipitate of cup*rous* cyanide, Cu_2Cy_2; soluble in excess, forming cuprous potassium cyanide, $Cu_2Cy_2,6KCy$ or $K_6Cu_2Cy_8$.

This double cyanide is also formed when excess of potassium cyanide is added to blue ammoniacal copper solution, the blue colour disappearing in consequence.

Sulphuretted hydrogen fails to precipitate copper sulphide from the solution of this double cyanide (*separation from cadmium*).

H_2S or **$(NH_4)_2S$** produces a nearly black precipitate of cupric sulphide, CuS, which, when exposed to the air in a moist condition, absorbs oxygen and is converted into the sulphate. *The precipitate is slightly soluble in ammonium sulphide.* It readily dissolves in potassium cyanide, forming cuprous potassium cyanide, $Cu_2Cy_2,6KCy$ (compare cadmium).

(*b*) **Cuprous Salts.**—The common cuprous salts are all insoluble in water. For the reactions, a solution of cuprous chloride in hydrochloric acid may be used.

KHO or **NaHO** gives a yellow precipitate of cuprous hydroxide, $Cu_2(HO)_2$ or Cu_2O,H_2O. If the mixture be heated, the precipitate is converted into the red cuprous oxide. The reduction of a cupric salt with the precipitation, the red cuprous

oxide, is brought about by many organic substances. Thus, if KHO be added to a solution of $CuSO_4$ in the presence of grape sugar, the $Cu(HO)_2$ first precipitated dissolves in excess of KHO to a blue solution. If this be gently warmed, a bright red precipitate of cuprous oxide Cu_2O is obtained.[1]

NH_4HO gives no precipitate, but forms a soluble compound having the composition $Cu_2Cl_2,2NH_3$. The solution is colourless, but rapidly absorbs oxygen from the air, first becoming brown, and finally depositing a greenish precipitate of cupric oxychloride, $CuCl_2,3CuO,4H_2O$.

SEPARATION OF THE METALS OF GROUP II., SUBDIVISION 1

Acidify the solution with a small quantity of dilute HCl,[2] and pass sulphuretted hydrogen through the liquid *until precipitation is complete.* The precipitate is then examined according to Table IIA. on the next page.

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[1] This reaction is utilised as a test for sugar. The reaction is more delicate when an alkaline solution of cupric tartrate (Féhling's solution) is employed.

[2] In the ordinary course of analysis HCl will already have been added for the separation of Group I., and most of the lead will have been precipitated. When the exercise is confined to Group II., if the addition of HCl gives a white precipitate, it should be filtered off and examined separately for lead.

TABLE IIA

SEPARATION OF THE METALS OF GROUP II. SUBDIVISION 1

The **precipitate** contains the sulphides of all the metals of the division. It should be well washed,[1] and then transferred to a small porcelain dish with the least possible quantity of water. About an equal volume of strong HNO_3 is then added, and the mixture boiled until no further dissolving action can be detected. The mixture is then diluted, and a few drops of dilute H_2SO_4 added. Before filtering, the mixture should be cooled.

The **residue** may contain HgS (*black*), $Hg(NO_3)_2,2HgS$ (*white*), and $PbSO_4$ (*white*). Boil with a solution of ammonium acetate.		The **filtrate** contains the nitrates of Bi, Cd, and Cu. Add excess of NH_4HO, and boil.	
The residue. Dissolve in the least quantity of *aqua regia.* Boil to expel chlorine, and neutralise with $NaHO$.[2] Acidify with HCl, and introduce a strip of clean copper, which will become coated with a silvery deposit of mercury.	**The solution.** Add K_2CrO_4. A yellow precipitate of $PbCrO_4$.	**The precipitate** is white Bi_2O_3,H_2O.[3] Confirm by dissolving in a few drops of HCl, and adding the solution drop by drop into a test-tube nearly filled with water. White BiOCl is precipitated.	**The solution** contains ammoniacal Cd and Cu compounds. The presence of Cu is seen by the blue colour. If blue, add KCy until colourless, and pass H_2S. Yellow CdS precipitated. _____ If copper is absent, H_2S may be added at once.

[1] Unless HCl (and soluble chlorides) be washed out of this precipitate, the addition of HNO_3 will result in the formation of a little *aqua regia,* and this will dissolve a portion of the mercuric sulphide.

[2] This step is necessary, in order to remove HNO_3, the presence of which might prevent the deposition of Hg.

[3] If any lead sulphate escaped precipitation in the previous step, or if any of the mercuric sulphide was dissolved (see previous note), compounds of these metals will be here thrown down by NH_4HO. Hence it is necessary to confirm Bi as indicated.

<div align="center">SUBDIVISION 2</div>

<div align="center">### Arsenic, As</div>

DRY REACTIONS.—Compounds of arsenic, when heated upon charcoal with Na_2CO_3 and KCy, are reduced; but the metal, being extremely volatile and readily combustible, is for the most part burnt to arsenious oxide, As_4O_6, which passes off as a white fume. At the same time some of the vapour of the element itself is carried away with the fumes of the oxide, and is readily recognised by its characteristic garlic-like odour.

The reduction may be made by heating the arsenic compound in a glass tube with KCy, or a mixture of Na_2CO_3 and KCy. The reaction is conveniently studied by using arsenious oxide. A small fragment (about the size of a pin's head) is placed in a narrow test-tube [2] and covered by adding a mixture of Na_2CO_3 and KCy (equal parts), the materials being as dry as possible. The total quantity of material in the tube should not occupy more space than is shown in Fig. 9. On the
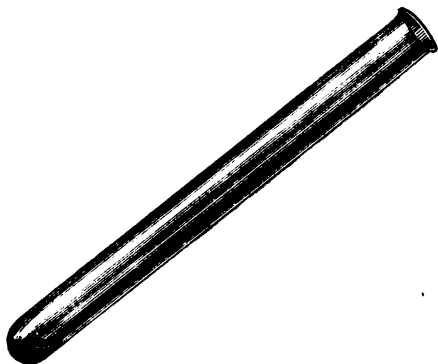
<div align="center">FIG. 9.</div>

application of a gentle heat, the first effect will be the expulsion of moisture from the imperfectly dried materials, which

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[1] For such experiments small test-tubes 4 × $\frac{5}{8}$ inches answer admirably. Bulb tubes are neither necessary nor desirable.

condenses upon the sides of the tube. This may be driven up the tube by gently warming it, and finally removed by introducing a " spill " of blotting-paper. When no more moisture collects, the mixture may be steadily heated in the tip of a small Bunsen flame. The arsenic sublimes upon the tube as a metallic mirror. Sufficient of the vapour escapes condensation to enable the strong garlic odour to be detected.

The reaction which takes place may be expressed by the equation—

$$As_4O_6 + 6KCy = As_4 + 6KOCy$$
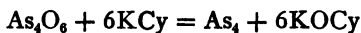
WET REACTIONS.—All the salts of arsenic are such as contain this element in the acidic or negative portion of the molecule; such, for example, as the arsenites and arsenates of various metals. No oxysalts of arsenic are known in which the element plays the part of a base.

(*a*) **Arsenious compounds,** derived from arsenious oxide, As_4O_6. The arsenites of sodium, potassium, and ammonium alone are soluble in water. For the following reactions, potassium arsenite, K_3AsO_3, or a solution of As_4O_6 in dilute HCl, may be employed.

H_2S or $(NH_4)_2S$ precipitates from slightly acid solutions yellow arsenious sulphide, As_2S_3. Soluble in excess of $(NH_4)_2S$, forming ammonium thio-arsenite, $(NH_4)_3AsS_3$.

It dissolves also in caustic alkalies, ammonia, and ammonium carbonate, yielding a mixture of arsenite and thio-arsenite, *e.g.*—

$$As_2S_3 + 6KHO = K_3AsO_3 + K_3AsS_3 + 3H_2O$$

On addition of an acid to such solutions, arsenious sulphide is precipitated.

When As_2S_3 is dissolved in yellow ammonium sulphide, ammonium thio-arsen*ate* is formed, and from this solution acids precipitate As_2S_5.

Arsenious sulphide is practically insoluble in HCl (*contrast* Sb_2S_3), but readily dissolves in HNO_3 or in HCl with the addition of a crystal of $KClO_3$.

CuSO$_4$ produces, in a solution of potassium arsenite, a

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green precipitate of hydrogen cupric arsenite, HCuAsO$_3$ (*Scheele's green*); soluble in ammonia and caustic alkalies. If the solution be boiled, the *arsenite* is oxidised to *arsenate* and cuprous oxide precipitated.

AgNO$_3$ gives a pale-yellow precipitate of silver arsenite, Ag$_3$AsO$_3$, soluble both in NH$_4$HO and in HNO$_3$. When the ammoniacal solution is boiled for some time, metallic silver is precipitated, and the *arsenite* is oxidised to *arsenate*.

Precipitation by Copper (Reinsch's test).—If a strip of clean copper foil be introduced into a solution of arsenious oxide in HCl, or an arsenite acidified with the same acid, and the mixture be warmed, metallic arsenic is deposited upon the copper, at the same time uniting with it, forming copper arsenide, Cu$_5$As$_2$. If the copper be then dried, and gently heated in a dry test-tube, the arsenic will be volatilised, and at the same time oxidised, giving, therefore, a white crystalline sublimate of As$_4$O$_6$ (*contrast antimony*).

(*b*) **Arsenic compounds,** derived from arsenic pentoxide, As$_2$O$_5$. Arsenates of sodium, potassium, and ammonium are soluble in water.

H$_2$S.—From acidified solutions of an arsenate, H$_2$S gives a yellow precipitate after a short time, which is either As$_2$S$_5$ or a mixture of As$_2$S$_3$ and S, depending upon conditions.

If the solution is strongly acid, and the gas is passed rapidly, the precipitate which slowly comes down is the penta-sulphide. On the other hand, if the solution is less strongly acid, and the H$_2$S is passed slowly, the arsenic acid is first reduced to arsenious acid, with deposition of sulphur, and the arsenious acid as it forms is converted into arsenious sulphide; thus—

$$\text{(1)} \quad H_3AsO_4 + H_2S = H_2O + S + H_3AsO_3$$
$$\text{(2)} \quad 2H_3AsO_3 + 3H_2S = As_2S_3 + 6H_2O$$
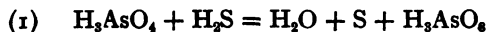
This reducing action of H$_2$S is very slow, therefore *complete precipitation requires considerable time.* Warming the liquid hastens the action. The addition of a more powerful reducing agent, such as sulphurous acid, produces the effect at once.

As$_2$S$_5$ dissolves in alkaline sulphides and in caustic alkalies,

forming thio-arsenates, from which the sulphide is reprecipitated by acids—

$$2K_3AsS_4 + 6HCl = 6KCl + As_2S_5 + 3H_2S$$
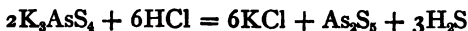
CuSO₄ gives a pale bluish precipitate of hydrogen cupric arsenate, $HCuAsO_4$. Soluble, like the corresponding arsenite, in ammonia; but the copper is not reduced on heating the solution, for the reason that arsenates are incapable of further oxidation—in other words, they do not act as reducing agents (*contrast arsenites*).

AgNO₃ produces a chocolate-coloured precipitate of silver arsenate, Ag_3AsO_4, which, like the arsenite, dissolves in NH_4HO and in HNO_3. The ammoniacal solution is not reduced on boiling, for the same reason that the copper salt is not reduced (*contrast arsenites*).

MgSO₄, in presence of NH₄Cl and NH₄HO, gives a white crystalline precipitate of ammonium magnesium arsenate, $(NH_4)MgAsO_4$; practically insoluble in water. (This reaction serves to *distinguish an arsenate from an arsenite.*)

Marsh's Test

In the presence of nascent hydrogen, both *arsenic* and *arsenious* compounds are reduced, and arsine (or arsenuretted hydrogen), AsH_3, is evolved. Thus, if a solution of arsenious or arsenic oxide be subjected to electrolysis, or if such solutions are introduced into a mixture from which hydrogen is being generated (*e.g.* zinc or magnesium with dilute acid), this compound is produced. The properties of arsenuretted hydrogen which are made use of in analysis are the following :—

(1) The deposition of metallic arsenic from the flame of the burning gas when a cold object is depressed upon the flame.

(2) The decomposition of the compound on passing through a heated tube, with deposition of an arsenical mirror.

(3) The action of the gas upon a solution of silver nitrate, resulting in the precipitation of metallic silver.

The reaction is made in a small hydrogen generating

apparatus, in which hydrogen is *slowly* generated from zinc and dilute sulphuric acid, both materials being free from arsenic. The issuing gas is passed through a piece of combustion tube which has been drawn out so as to produce one or two constricted places in its length, as shown in Fig. 10. As soon as the air is all expelled from the apparatus, the issuing hydrogen is inflamed.[1]
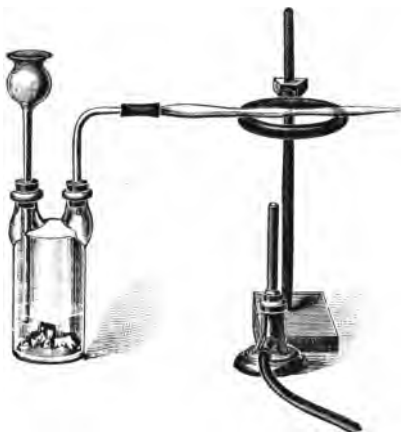
FIG. 10.

A small quantity of the arsenical solution is now introduced through the thistle-tube. The first effect of this is to suddenly cause a greatly increased rate of evolution of hydrogen.[2] The colour of the hydrogen flame will be seen to change, and to assume a lilac tint, and at the same time white fumes of As_4O_6 escape from the tip of the flame. If now a porcelain dish be depressed upon the flame, a rich brown-black metallic-looking stain will be deposited. The deposit being volatile, and the flame very hot, the stain will again disappear if the flame be allowed to impinge for more than a moment or two on the same spot.

If the drawn-out tube be heated near one of the constrictions, the arsenuretted hydrogen will be decomposed as it passes the

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[1] A small test-tube should be filled by upward displacement, and tested by a flame before igniting the gas at the exit-tube of the apparatus. As an additional precaution, it is well to throw a duster lightly over the bottle before applying a light, so that, should an explosion happen, the broken glass will be prevented from flying about.

[2] On this account, it is necessary that the generation of hydrogen *before* adding the arsenic solution should be quite slow ; and also that the quantity of the arsenic solution added at a time should be small.

hot spot, and an arsenic mirror will be deposited in the tube. Minute traces of arsenic can be detected in this way.

It will be noticed that the deposition takes place entirely on that part of the tube which is on the side of the flame farthest from the generating vessel (antimony is deposited from its hydride on *both sides* of the heated spot).

Since antimony also forms a gaseous compound with hydrogen which gives similar stains, it is necessary to employ further confirmatory tests.

1. The arsenic stains are readily dissolved by a solution of a hypochlorite. If, therefore, a solution of bleaching powder be poured over such stains they immediately disappear—

$$5Ca(OCl)_2 + 6H_2O + As_4 = 5CaCl_2 + 4H_3AsO_4$$

Antimony stains do not dissolve in hypochlorite solutions.

2. When a stream of H_2S is passed through the tube containing the deposit of either arsenic or antimony, slightly warmed, in each case the sulphide is formed. Yellow arsenious sulphide volatilises along from the warm region and condenses on the cold distant part of the tube; antimonious sulphide, reddish or nearly black, remains unmoved, being non-volatile. (If present together, they can in this way be separated.)

If a stream of gaseous HCl be now passed through the tube, antimonious sulphide is converted into antimonious chloride, which passes on with the HCl, and may be led into water and again precipitated as the red sulphide with H_2S. The yellow arsenious sulphide remains in the tube, being unattacked by HCl.

3. Arsenuretted hydrogen can also be distinguished from the antimony compound, by the difference in the behaviour of the two gases towards silver nitrate. When passed into the silver solution, each gas produces a black precipitate. In the case of arsenic this consists of metallic silver, while with antimony it consists of antimonide of silver; thus—

$$6AgNO_3 + 3H_2O + AsH_3 = 3Ag_2 + 6HNO_3 + H_3AsO_3$$
$$3AgNO_3 + SbH_3 = SbAg_3 + 3HNO_3$$
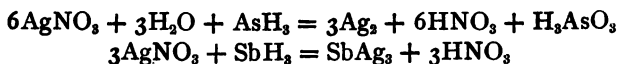
On filtering, the arsenic is found in the filtrate, while the antimony

would be in the precipitate. If the filtrate is neutralised by the cautious addition of ammonia, a yellow precipitate of silver arsenite is produced by interaction with the excess of silver nitrate present.

The antimony in the black silver antimonide may be detected by boiling with a solution of tartaric acid. The liquid thus obtained is acidulated with HCl, and sulphuretted hydrogen passed into it, which gives a precipitate of red antimonious sulphide.

Fleitmann's Test

When an arsenite, or a solution of arsenious oxide, is warmed in a test-tube with a solution of sodium hydroxide and metallic zinc, arsenuretted hydrogen is evolved, which can be detected by means of a piece of filter-paper moistened with silver nitrate held to the mouth of the tube. A black stain of precipitated silver is produced. Antimoniuretted hydrogen is not produced from antimony compounds under similar conditions.

Antimony, Sb

DRY REACTIONS.—Antimony compounds may be reduced to metallic antimony by heating them with Na_2CO_3 and KCy upon charcoal. Globules of the metal are thus obtained, which burn in the blowpipe flame, producing white fumes of antimonious oxide, Sb_4O_6. The charcoal at the same time receives a white incrustation. The bead of metal will be found to be very brittle, and, when broken, to exhibit a highly crystalline appearance. Antimony is unacted upon by dilute HCl or H_2SO_4. Nitric acid oxidises it into antimonic acid, or antimonious oxide, depending upon conditions of concentration.

WET REACTIONS.—Antimony forms two series of compounds, "antimonious" and "antimonic," which may be regarded as being derived respectively from the two oxides, antimonious oxide, Sb_4O_6, and antimony pentoxide, Sb_2O_5.

(*a*) **Antimonious Compounds.**—Antimonious oxide is feebly basic, forming salts in which the metal constitutes a part of the positive radical. Of these salts the tartrate, $(SbO)_2(C_4H_4O_6)$, and

the double potassium tartrate (*tartar emetic*), $(SbO)K(C_4H_4O_6)$, are the most familiar. For the following reactions[1] an acid (HCl) solution of antimonious chloride may be employed :—

KHO, NaHO, NH_4HO, as well as alkaline carbonates, precipitate antimonious oxide, Sb_4O_6.

The precipitate redissolves in excess of either potassium or sodium hydroxide, forming the respective metantimonites—

$$Sb_4O_6 + 4NaHO = 4NaSbO_2 + 2H_2O$$
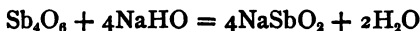
H_2O, added in considerable quantity to the acid solution of $SbCl_3$, gives a white precipitate of an oxychloride, SbOCl. The precipitate dissolves in tartaric acid forming antimonyl tartrate, $(SbO)_2(C_4H_4O_6)$ (*distinction from bismuth*).

H_2S and $(NH_4)_2S$ give a red or orange-red precipitate of antimonious sulphide, Sb_2S_3, soluble in excess of ammonium sulphide forming ammonium thio-antimonite. It dissolves also in caustic alkaline, and from all these solutions Sb_2S_3 is reprecipitated on addition of HCl.

When dissolved in yellow ammonium sulphide it forms ammonium thio-antimon*ate*, and from this solution acids precipitate Sb_2S_5.

Antimonious sulphide is not dissolved by ammonia or by ammonium carbonate (*contrast arsenic*).

Antimonious sulphide is decomposed by hot hydrochloric acid, with evolution of sulphuretted hydrogen (*contrast arsenic*)—

$$Sb_2S_3 + 6HCl = 2SbCl_3 + 3H_2S$$
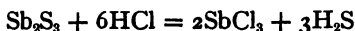
(*b*) **Antimonic Compounds.**—These are derived from the pentoxide, Sb_2O_5, the pyro-antimonates (*e.g.* $K_4Sb_2O_7$) and metantimonates (*e.g.* $KSbO_3$) being the most familiar salts.

Potassium pyro-antimonate is readily soluble in water, while the sodium salt is difficultly soluble, hence the potassium compound is used as a reagent for sodium (p. 23).

H_2S and $(NH_4)_2S$ produce with acidified solutions of antimonic compounds an orange-red precipitate consisting of Sb_2S_5, Sb_2S_3, and S in varying proportions.

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[1] Except that with $AgNO_3$, in which obviously the presence of chlorine would interfere.

The precipitate dissolves in alkaline sulphides and caustic alkalies, and from these solutions Sb_2S_5 is reprecipitated by HCl.

Precipitation of Metallic Antimony.—If one or two drops of an antimony solution acidified with HCl are placed upon a piece of clean platinum foil, and a small fragment of zinc immersed in the liquid, a black stain is produced upon the platinum by the deposition of metallic antimony. HCl has no action upon the deposit (*distinction from tin*).

Antimoniuretted hydrogen is evolved when antimony compounds are acted upon by nascent hydrogen. The compound undergoes reactions similar to those of the corresponding arsenic compound. The methods for distinguishing between them are described under arsenic.

Tin, Sn

DRY REACTIONS.—Compounds of tin are reduced to the metallic state by being heated on charcoal with Na_2CO_3 and KCy in the reducing flame. A portion of the metal is oxidised by the flame, and produces a white incrustation of SnO_2 upon the charcoal; this, on being moistened with cobalt nitrate, and reheated, assumes a greenish appearance.

The beads of reduced metal are malleable (therefore easily distinguished from Bi or Sb), but are not soft enough to mark paper in the manner of lead.

The metal dissolves in hot strong HCl, forming stannous chloride, $SnCl_2$. Strong nitric acid converts it into white insoluble metastannic acid, $(H_2SnO_3)_5$.

WET REACTIONS.—Tin forms two classes of compounds, distinguished as " stannous " and " stannic," derived respectively from stannous oxide, SnO, and stannic oxide, SnO_2.

(*a*) **Stannous Compounds.**—Of these the chloride, sulphate, and nitrate are soluble in water.

HKO, NaHO, NH_4HO, as well as alkaline carbonates, give with stannous chloride a white precipitate of hydrated stannous oxide (basic hydroxide); thus—

$$2SnCl_2 + 4KHO = 2SnO,H_2O + 4KCl + H_2O$$

The precipitate is soluble in excess of KHO or NaHO (but not in the other precipitants), forming alkaline *stannites ;* thus—

$$2SnO,H_2O + 4KHO = 2K_2SnO_2 + 4H_2O$$
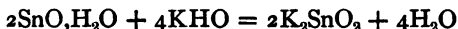
H_2S or $(NH_4)_2S$ gives, with dilute solutions of stannous chloride, a deep brown precipitate of stannous sulphide; soluble in caustic alkalies, but reprecipitated on acidification. Soluble also in yellow ammonium sulphide forming the thio-stann*ate.*

Stannous sulphide is insoluble in colourless ammonium sulphide and in ammonium carbonate. Boiling HCl converts it into $SnCl_2$; while *aqua regia* oxidises it to stannic chloride, $SnCl_4$.

Oxidation of Stannous Compounds.—These substances readily pass, by oxidation, into stannic compounds ; they therefore act the part of powerful *reducing* agents in a number of reactions, of which the following are important :—

(1) **Mercuric chloride,** see Reactions for Mercury, p. 56.

(2) **Ferric salts** are reduced to the "ferrous" state ; thus, ferric sulphate, in the presence of hydrochloric acid, gives ferrous sulphate and stannic chloride—

$$Fe_2(SO_4)_3 + SnCl_2 + 2HCl = 2FeSO_4 + H_2SO_4 + SnCl_4$$
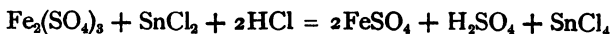
(3) **Gold chloride,** in the presence of acid, is reduced to metallic gold—

$$2AuCl_3 + 3SnCl_2 = 3SnCl_4 + 2Au$$
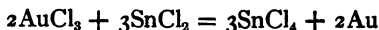
In dilute *neutral* solutions, a reddish or purple coloration is produced, known as *purple of Cassius.*

(*b*) **Stannic Compounds.**—Stannic oxysalts, such as the nitrate or sulphate, are unstable, being converted by water into insoluble metastannic acid ; and as stannic oxide, SnO_2, is insoluble in HCl, a stannic solution for the following reactions is best obtained by oxidising an HCl solution of stann*ous* chloride either by adding bromine water to it, or by warming with a crystal of $KClO_3$.

HKO, NaHO, NH_4HO, as well as alkaline carbonates, give

a white precipitate of hydrated stannic oxide, or stannic acid, SnO_2,H_2O, or H_2SnO_3; thus—

$$SnCl_4 + 4NaHO = H_2SnO_3 + 4NaCl + H_2O$$

Soluble in HNO_3 and in HCl. Soluble in KHO and NaHO, with formation of the respective stannates, K_2SnO_3 and Na_2SnO_3; thus—

$$H_2SnO_3 + 2NaHO = Na_2SnO_3 + 2H_2O$$
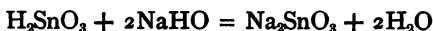
H_2S or $(NH_4)_2S$ precipitates yellow stannic sulphide, SnS_2 (with H_2S the precipitate appears nearly white at first, and is only complete in dilute solutions). The precipitate is soluble in caustic alkalies, in ammonium sulphide, and sulphides of the alkalies, forming thio-stannates; thus—

$$3SnS_2 + 6KHO = 2K_2SnS_3 + K_2SnO_3 + 3H_2O$$
$$SnS_2 + (NH_4)_2S = (NH_4)_2SnS_3$$
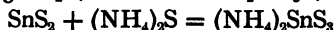
From these solutions the yellow stannic sulphide is reprecipitated on the addition of HCl—

$$(NH_4)_2SnS_3 + 2HCl = 2NH_4Cl + SnS_2 + H_2S$$
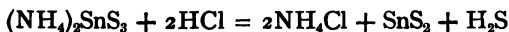
Stannic sulphide is insoluble in ammonium carbonate, but dissolves in hot strong HCl.

Precipitation of Metallic Tin.—When zinc is immersed in an acid solution of stannous or stannic chloride, the tin is precipitated as a grey-black deposit upon the zinc; or, if the whole of the zinc becomes dissolved, the tin is left as a scaly powder. It dissolves in warm HCl (*contrast antimony*).

Separation of Group II. into Subdivisions 1 and 2

The solution, if neutral or alkaline, is acidified with HCl,[1] and sulphuretted hydrogen passed through until the precipitation of all the metals of Group II. is complete. The precipitate is washed and is then transferred to a small beaker, and gently

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[1] If the solution under examination is alkaline, it may contain thio-salts of As, Sb, or Sn; the addition of HCl will result in the precipitation of the sulphides of these metals. If it is neutral, basic salts of antimony might be precipitated at first, but redissolve on warming with a slight excess of the acid.

warmed with yellow ammonium sulphide for a few minutes. The liquid is then filtered. The residue consists of the undissolved sulphides of the metals of subdivision 1, the filtrate contains the thio-salts of the metals of subdivision 2.

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[1] Ammonium sulphide dissolves CuS to a slight extent (see Reactions, p. 61), hence, if this element is present, a small quantity of it may find its way into the solution along with As, Sb, and Sn.

TABLE IIB

SEPARATION OF THE METALS OF GROUP II, SUBDIVISION 2

The solution contains the thio salts of As, Sb, and Sn. It should be somewhat diluted, and hydrochloric acid added drop by drop until the sulphides are completely reprecipitated; then filtered and washed. The precipitate is then transferred to a boiling-tube with a small quantity of HCl, and boiled for a few moments until H_2S is no longer given off. It is then diluted and filtered.

The **residue** consists of arsenic sulphide and sulphur.	The **solution.** Pour a few drops upon a piece of platinum foil, and add a fragment of zinc. A black stain indicates Sb. If antimony is present, place a strip of zinc along with the platinum foil in the remainder of the solution, until all the antimony and tin are thrown down. Collect the deposit and boil it with strong HCl, and filter. Test the filtrate for Sn by means of $HgCl_2$.
Confirm by dissolving in HCl with a crystal of $KClO_3$, and applying special reactions for arsenic, such as Fleitmann's or Reinsch's test.[1]	

[1] In order to ascertain the condition of oxidation in which the arsenic originally existed in the substance under analysis, special tests must be applied to the solution before it has been exposed either to reducing or oxidising influences, as in the case of iron.

CHAPTER VIII

REACTIONS OF THE METALS OF GROUP 1

Silver, Ag

DRY REACTIONS.—Compounds of silver, when heated on charcoal with sodium carbonate in the reducing flame, yield metallic silver; which, being non-oxidisable, is not accompanied by any oxide incrustation upon the charcoal. The metal, however, is slightly volatile in the blowpipe flame, and sometimes a faint red-brown incrustation is thus obtained.

The reduced metal may be removed to a watch-glass, dissolved in nitric acid, and precipitated as chloride.

WET REACTIONS.—Of the common salts of silver, the nitrate is readily soluble, the acetate and sulphate sparingly soluble, in water.

HCl, and soluble chlorides, give a white curdy precipitate of silver chloride, AgCl, which, on being warmed or stirred, becomes granulated in appearance, and very quickly settles. On exposure to light, the white compound assumes a slate colour or drab tint, which gradually deepens to a violet, and finally appears brown or black.

Silver chloride is quite insoluble in water and in nitric acid. It is soluble to a slight extent in strong HCl, but reprecipitated completely on dilution. It readily dissolves in ammonia, forming the compound $2AgCl,3NH_3$, but reprecipitated on the addition of nitric acid.

Silver chloride is soluble also in KCy, being first converted into siver cyanide, which dissolves in excess of KCy, forming the double cyanide KCy,AgCy. It also dissolves in sodium

thiosulphate, with the formation of a double thiosulphate; thus—

$$AgCl + Na_2S_2O_3 = NaCl + NaAgS_2O_3$$
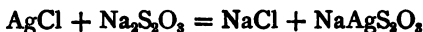
[Reactions with bromides, iodides, and cyanides are described under the respective acids.]

KHO, NaHO, or NH₄HO gives a greyish-black precipitate of silver oxide, Ag_2O. Insoluble in excess of the caustic alkalies, but readily soluble in ammonia.

H₂S or (NH₄)₂S produces a black precipitate of silver sulphide, Ag_2S. Insoluble in dilute acids, except boiling dilute nitric acid, which converts it into nitrate.

Silver sulphide is insoluble in ammonia, ammonium sulphide, or potassium sulphide.

Reduction of Silver Salts.—Silver compounds are readily reduced to the metallic state; for example, if silver chloride is placed in a little dilute sulphuric acid, and strip of zinc introduced, the nascent hydrogen converts the white chloride into grey metallic silver. The reduction is complete when a particle of the grey solid dissolves completely in nitric acid.

Lead, Mercury

The reactions of these metals have already been considered in connection with the metals of Group II., Subdivision 1, pp. 54, 57.

TABLE I

SEPARATION OF THE METALS OF GROUP I

To the solution add moderately dilute hydrochloric acid drop by drop, until a slight excess beyond what is required for complete precipitation has been added. Gently warm the mixture,[1] and after again cooling it[2] filter. The filtrate contains Groups II, III, IV, and V.

The **precipitate**, consisting of $PbCl_2$, $AgCl$, and Hg_2Cl_2, is thoroughly washed in cold water, and then boiled with water (or washed while in the filter with boiling water) and filtered.

The **filtrate** contains $PbCl_2$, which deposits in white needle-shaped crystals on cooling.	The **residue** is treated, while still upon the filter, with a small quantity of ammonia, which dissolves the AgCl, and converts the white Hg_2Cl_2 into black $NH_2(Hg_2)Cl$.
Confirm by special test, *e.g.* the formation of $PbCrO_4$.	The solution yields a white precipitate of AgCl upon being acidified with HNO_3.
	The black residue may be dissolved in a little *aqua regia*, and (after being nearly neutralised) the mercury precipitated upon metallic copper.

[1] The first addition of HCl may precipitate basic salts of antimony, warming with excess of the acid ensures their re-solution.

[2] Unless cooled the lead chloride may all remain dissolved.

GENERAL TABLE FOR THE SEPARATION

To the solution of the substance under analysis (see pp. 112, *et seq.*) add a few
ployed in effecting the solution of the substance, this first step in the general
reagent gradually until the precipitation is complete.　Warm gently

The **Precipitate** may consist of—	The **Filtrate** is gently warmed, and a stream of sulphuretted cipitation is complete (watch the precipitation carefully,	
AgCl Hg$_2$Cl$_2$ PbCl$_2$ —— Group I. Examine by Table I. (p. 79).	A small portion of the mixture should be filtered, and the etted hydrogen passed into it.　Should any further pre-filtered, and treated to more gas.	
	The **Precipitate** may consist of— (1) PbS ; HgS ; Bi$_2$S$_3$; CuS ; CdS. (2) Sb$_2$S$_3$; As$_2$S$_3$; SnS ; SnS$_2$. Wash thoroughly, and then transfer it to a small beaker and warm gently with yellow ammonium sulphide.　See Note 3.	The **Filtrate**. Boil until sul-and boil again for a few the sulphuretted hydrogen), the extent to which it has liminary tests, the evapora-to destroy the latter, and Test a small portion of the To the main portion of the NH$_4$HO until precipitation
		The Precipitate. I. *In the absence of phosphoric acid*, may consist of— Al$_2$(HO)$_6$; Cr$_2$(HO)$_6$; Fe$_2$(HO)$_6$. Examine by Table IIIA. (p. 41).

| | The **Residue** may contain the sulphides of Division I.

Examine by Table IIA. (p. 63). | The **Filtrate** may contain the thio salts of As, Sb, Sn.

Examine by Table IIB. (p. 76). | |

II. *In the presence of phosphoric acid*, besides the above hydroxides, the precipitate may contain the phosphates of any or all of the metals of Groups III. and IV., and of magnesium.

Examine by Table IIIc. (p. 52).

drops of dilute HCl. [Obviously in cases when HCl has already been em-
separation is omitted.] If any precipitate is produced, continue adding the
(see footnote, p. 74), then thoroughly cool again, and filter.

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hydrogen slowly bubbled through the liquid, with frequent stirring, until pre-
and note any colour changes). See Note 2, following page.

filtrate diluted with two or three times its volume of water, and more sulphur-
cipitation result, the main portion must be similarly diluted, without being

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phuretted hydrogen is entirely expelled. Add two or three drops of HNO_3,
moments (to oxidise any iron or chromium which may have been reduced by
and then evaporate the liquid to about half its volume, or less, according to
become diluted. If silica or organic compounds have been detected by pre-
tion must be carried down to dryness, and the residue gently heated in order
render the silica insoluble. The residue is then extracted with HCl and water.
solution for phosphoric acid (see p. 51).
solution add a considerable quantity of NH_4Cl, and heat to boiling. Add
is complete (see p. 40), boil for a moment, and filter while hot.

The Filtrate. Pass sulphuretted hydrogen (or add ammonium sulphide) until
precipitation is complete. Gently warm the liquid (see Ni, p. 47), and filter.

The **Precipitate** may consist of— MnS ; ZnS ; NiS; CoS. Examine by Table IIIB. (p. 50).	The **Filtrate.** Boil to expel H_2S. If ammonium sulphide has been employed, add a little HCl before boiling. If necessary, concentrate the solution by evaporation. Add NH_4HO until alkaline, and $(NH_4)_2CO_3$ until precipitation is complete. Warm the liquid, but do not boil (see p. 30).

The **Precipitate** may consist of— $BaCO_3$; $SrCO_3$; $CaCO_3$. Examine by Table IV. (p. 31).	The **Filtrate.** Examine for Mg, K, Na, by Table V. (p. 27). ——— NOTE 1.—In testing for Mg at this point, it will obviously be unnecessary to add *more* NH_4Cl and NH_4HO. NOTE 2.—Any failure to effect *complete* group separations will usually result in the precipita- tion of some metallic phosphate at this stage, other than magnesium phosphate.

G

Notes on the General Table of Separation

1. Take great care to ensure *complete precipitation* in every group separation, otherwise the object of the separation is defeated. For the same reason every group precipitate should be *thoroughly washed* to free it from adhering solution which contains groups that follow. Such washings need not be mixed with the first filtrates, otherwise the liquid becomes too much diluted.

2. To ensure complete precipitation here it is necessary that the solution be not too strongly acid (hence unnecessary excess of HCl in precipitating Group I. must be avoided). See Cd, p. 60 ; also As, p. 66.

3. Copper sulphide is slightly soluble in ammonium sulphide (see p. 61). An alternative reagent which may be employed is caustic soda ; this does not dissolve CuS, but it dissolves HgS more freely, hence cannot be used unless mercury is known to be absent—ascertained by the preliminary tests. When both copper and mercury are present ammonium sulphide should be used.

THE NEGATIVE OR ACID RADICALS

THESE are the negative ions (*anions*) which are produced when the acids (hydrogen salts) or salts (metallic salts) undergo dissociation when dissolved in water. Thus, the negative radical in hydrochloric acid or in metallic chlorides is the chloride ion, $\overline{Cl}$; the tests for chlorides, therefore, are tests for this ion. Similarly, sulphates and nitrates dissociate into their positive ions, and the negative ions $\overline{SO}_4$ and $\overline{NO}_3$ respectively; the tests for sulphuric and nitric acids are thus, in reality, tests for these negative ions, although, in ordinary language, we often speak of them as tests for the various *acids* from which these ions are derived. The negative radicals are classified into groups on the basis of their behaviour towards certain chosen reagents, but these reagents are not employed as group-reagents to *separate* one group of acid radicals from another, but are merely used in order to discover, by a single operation, the absence or otherwise of an entire group, whereby the necessity for applying a number of separate tests may be obviated.

The acids which will be included in this section are the following :—

Hydrochloric acid, Chloric acid.
Hydrobromic acid.
Hydriodic acid.
Hydrofluoric acid.
Sulphuretted hydrogen, Sulphuric acid, Sulphurous acid.
Nitric acid, Nitrous acid.
Phosphoric acid.
Carbonic acid.
Silicic acid.
Boric acid.

Certain acids, such as Arsenious, Arsenic, Chromic, Permanganic, have already been discussed under their respective metals.

Hydrochloric Acid and Chlorides

Hydrogen chloride is a colourless gas having a sharp choking smell. It fumes in contact with moist air, is strongly acid, but has no bleaching properties. It is extremely soluble in water, the solution constituting the ordinary reagent, hydrochloric acid.

The chlorides are all soluble in water, except those of the metals of Group I. ($PbCl_2$ being soluble in hot water), and certain others which are decomposed by water, such as the chlorides of antimony, bismuth, and tin.

Silver nitrate, $AgNO_3$, gives, in solution of chlorides or hydrochloric acid, a white precipitate of silver chloride. Insoluble in nitric acid. Readily soluble in ammonia, even dilute (for further properties, see Silver reactions, p. 78).

AgCl is distinguished from either AgBr or AgI by the fact that chlorine water is without action upon it (see Bromides and Iodides). It may also be distinguished in the following way :—
If the washed precipitate of AgCl be mixed with a little very dilute sulphuric acid, and a strip of zinc placed in the mixture, the silver chloride turns grey, owing to its reduction to metallic silver, while zinc chloride passes into solution. This, on treatment with manganese dioxide and sulphuric acid, will yield chlorine.

Fusion with sodium carbonate converts AgCl into metallic silver and sodium chloride. On treatment with water, chlorine can be liberated from the solution, as in the foregoing.

Liberation of Chlorine from Chlorides.—The chloride is mixed with MnO_2 and H_2SO_4, and the mixture gently warmed in a test-tube. The chlorine which escapes may be detected by its characteristic smell and by its bleaching properties (litmus paper, or, better, paper coloured red by an alkaline solution of carmine, may be used). Small quantities may be detected by fitting the test-tube with a cork and delivery tube, and passing the evolved gas into water in a second tube. The

presence of free chlorine in the water may be detected by adding a few drops of Kl solution and then starch paste. A blue coloration results from the liberated iodine (set free by the chlorine) uniting with the starch.

Liberation of Hydrogen Chloride.—When chlorides (except those of tin, lead, mercury, and silver) are gently heated with strong H_2SO_4, hydrogen chloride is evolved.

The presence of hydrochloric acid in a solution containing a soluble chloride may be detected by gently warming the liquid with MnO_2 (without sulphuric acid), when chlorine is evolved, which may be detected as described above—

$$4HCl + MnO_2 = MnCl_2 + 2H_2O + Cl_2$$

Formation of Chromyl Chloride.—When a mixture of a chloride and potassium dichromate is gently warmed with strong sulphuric acid, a red-brown vapour is disengaged (resembling bromine in colour, but very different in smell) consisting of chromyl chloride, CrO_2Cl_2—

$$4KCl + K_2Cr_2O_7 + 3H_2SO_4 = 3K_2SO_4 + 3H_2O + 2CrO_2Cl_2$$
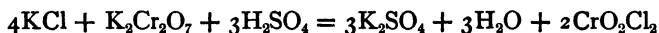
If the reaction be made in a test-tube fitted with a delivery tube, and the vapour of the chromyl chloride be passed into a second test-tube containing an alkaline hydroxide, a chromate of the alkali is formed—

$$CrO_2Cl_2 + 4NH_4HO = (NH_4)_2CrO_4 + 2NH_4Cl + 2H_2O$$

The presence of the chromate is indicated by the yellow colour which the liquid assumes, which may be confirmed by acidifying with acetic acid and adding lead acetate. The presence of the chromate is proof of the presence of a *chloride* in the first test-tube.

By means of this test it is possible to detect a chloride *in the presence of* either a bromide or iodide,[1] as neither bromine nor iodine form similar chromyl compounds.

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[1] The former tests (p. 84), which enable one to *distinguish between* a chloride, bromide, and iodide, will not be confounded with a test such as

Hydrobromic Acid and Bromides

Gaseous hydrobromic acid closely resembles hydrochloric acid. The properties of the gas are not used in analysis.

All bromides are soluble in water, except mercurous bromide and silver bromide; lead bromide dissolves in boiling water less easily than the chloride.

Silver nitrate, $AgNO_3$, precipitates from solutions of bromides or hydrobromic acid, pale-yellow silver bromide, $AgBr$ (the colour is indistinguishable from white by gaslight). It is insoluble in nitric acid, and difficultly soluble in ammonia (scarcely soluble in dilute ammonia. *Contrast* $AgCl$).

$AgBr$ may be distinguished from $AgCl$ by shaking up a little of the washed precipitate with a few drops of carbon disulphide and chlorine water.

Silver bromide is decomposed by metallic zinc in the presence of dilute sulphuric acid, in the same manner as the chloride. Zinc bromide goes into solution, from which the bromine can be separated by either of the methods given below.

Prolonged boiling with a strong solution of sodium carbonate (or, better, heating the dry substances strongly in a glass tube) decomposes silver bromide. On filtering (after extraction with water in the case of the *dry* reaction), the aqueous solution containing sodium bromide may be tested as above.

Liberation of Bromine from Bromides.—When gently warmed with MnO_2 and H_2SO_4, bromides evolve bromine, which escapes as a brown-red vapour having an irritating smell, condensing on a cold surface to dark brown-red drops of liquid. In contact with starch, it gives a yellow colour; if, therefore, the reaction is made in a small beaker which is covered with a piece of moistened filter-paper upon which a starch flour is dusted, this yellow colour is produced.

Bromine is also liberated by means of chlorine. By adding

the above, which permits of the detection of one class of salts *in the presence of* others.

chlorine water to a solution of a bromide, the liquid becomes brownish; and if a little carbon disulphide is added and the mixture shaken, the bromine is taken up by the disulphide, which settles down as a brown layer at the bottom.

By this reaction a bromide can be detected in the presence of a chloride.

When bromides (except Hg_2Br_2 and AgBr) are acted upon with strong sulphuric acid, bromine is liberated along with hydrobromic acid and sulphur dioxide—

$$KBr + H_2SO_4 = HBr + HKSO_4$$
$$2HBr + H_2SO_4 = Br_2 + SO_2 + 2H_2O$$
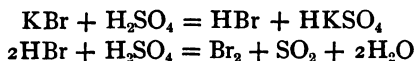
The detection of hydrobromic acid in solution in presence of a dissolved bromide is accomplished by gently warming the liquid with MnO_2. Bromine is liberated from the acid (not from the bromide), and may be detected by the starch test.

Hydriodic Acid and Iodides

Gaseous hydriodic acid closely resembles HBr and HCl. The properties of the gaseous compound are not utilised in analysis.

All iodides are soluble in water except those of silver, mercury, copper (gold, platinum, and palladium). Those of bismuth and lead are sparingly soluble.

Silver nitrate, $AgNO_3$, precipitates from solutions of iodides or hydriodic acid a pale-yellow precipitate of silver iodide, AgI, insoluble in HNO_3, and more difficult of solution in NH_4HO than AgBr. AgI may be distinguished from either AgBr or AgCl by shaking up the precipitate with a little CS_2 and chlorine water.

Copper sulphate, $CuSO_4$, gives a dirty white precipitate of cuprous iodide, Cu_2I_2, coloured by free iodine. In presence of suitable reducing agents, such as sulphurous acid, the whole of the iodine is precipitated as white Cu_2I_2. Bromides and chlorides give no precipitate with $CuSO_4$, hence by this

reaction an iodide may be *separated* from a mixture of halogen salts.

Liberation of Iodine from Iodides.—Iodine is more easily set free from combination than either bromine or chlorine, and the methods which are applicable for the liberation of these apply also in the case of iodine. Thus, manganese dioxide and dilute sulphuric acid decompose iodides in a manner precisely similar to that explained on p. 84 for chlorides. Strong acids, as nitric and sulphuric, also expel iodine from iodides, with evolution of oxide of nitrogen, or sulphur dioxide ; *e.g.*—

$$2KI + 2H_2SO_4 = K_2SO_4 + 2H_2O + SO_2 + I_2$$

The comparative ease with which iodine is liberated from combination, affords the basis of most of the tests by which this element is detected. . The following are the reactions most used in analysis :—

1. **Chlorine water,** when added to a solution of an iodide, expels the iodine. The test may be applied as described under bromine, the carbon disulphide in this case being coloured violet.

The presence of the liberated iodine may also be recognised by means of starch. A small quantity of starch paste is mixed with the solution of the iodide, and one or two drops of chlorine water added, when the deep indigo-blue compound of iodine with starch is produced. On the addition of an excess of chlorine, the colour is destroyed. Boiling the liquid also destroys the compound, hence, when small quantities of iodine are being tested, it is necessary to avoid using the starch while hot.

2. **Nitrous Acid.**—When a solution of an iodide is acidified with dilute sulphuric acid, and a few drops of a solution of sodium nitrite added, the nitrous acid generated (by the action of the acid upon the nitrite) decomposes the iodide, with the liberation of iodine. The action is in reality between the nitrous acid and hydriodic acid ; thus—

$$HNO_2 + HI = H_2O + NO + I$$
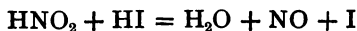
Neither chlorine nor bromine is liberated by nitrous acid.

Detection of Bromides and Iodides in Solution together.—When carbon disulphide is added to a solution of an iodide and bromide in a test-tube, and chlorine water added in *small* quantities at a time, with agitation, the iodine will be liberated first. If this be done carefully, it is not difficult to see when the further addition of a drop of chlorine water produces no further precipitation of iodine. At this point the carbon disulphide is coloured deep violet with dissolved iodine. A portion of the aqueous liquid is then withdrawn by means of a small pipette and transferred to another test-tube. A fresh quantity of carbon disulphide is now added to this, and a few drops of chlorine water. If the whole of the iodine had been liberated in the first tube, the bromine now begins to be expelled, and the carbon disulphide becomes brown. If a small quantity of iodine were still left, the first drop of chlorine water causes its liberation, and, on shaking, the disulphide will show a pale-violet colour. A few more drops of chlorine water, however, will destroy this, and afterwards liberate the bromine.

Detection of Iodides, Bromides, and Chlorides in Solution together.— The solution containing the three salts, to which a little carbon disulphide has been added, is acidified with two or three drops of dilute sulphuric acid, and a dilute solution of sodium nitrite added drop by drop until the whole of the iodine has been liberated. On shaking the mixture this will be dissolved by the carbon disulphide, giving the violet solution. The aqueous liquid is then withdrawn with a pipette and divided into two portions. The first is neutralised by the cautious addition of ammonia drop by drop. It is then shaken with chlorine water and carbon disulphide. The bromine is thereby liberated, and imparts its brownish colour to the disulphide. The second portion is evaporated down, mixed with potassium dichromate and sulphuric acid, and the chromyl-chloride test made as described on p. 85.

Chloric Acid and Chlorates

Chloric acid is unstable except in dilute solutions.

The chlorates are all soluble in water, therefore no reagents give precipitates by double decomposition. They are all decomposed by heat, evolving oxygen (in some cases mixed with chlorine), and leaving either a metallic chloride or oxide.

When heated with oxidisable substances (*e.g.* charcoal), deflagration of the mixture results.

Hydrochloric acid decomposes chlorates, with the evolution of chlorine and chlorine peroxide—

$$4KClO_3 + 12HCl = 4KCl + 6H_2O + 9Cl + 3ClO_2$$

(The use of this mixture as an oxidising agent has frequently been referred to.)

Sulphuric acid decomposes chlorates, with the evolution of chlorine peroxide (a deep yellow unpleasant-smelling gas), which on very slight elevation of temperature, explodes with violence—

$$3KClO_3 + 2H_2SO_4 = KClO_4 + 2HKSO_4 + H_2O + 2ClO_2$$
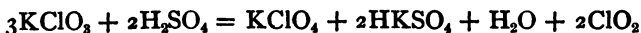
On adding a few drops of strong sulphuric acid to a small crystal of potassium chlorate, the mixture immediately becomes yellow, and on very gently warming explodes with a sharp detonation. This is characteristic of chlorates.

Separation of a Chloride and Chlorate.—Add a solution of silver sulphate; this precipitates silver chloride, which is removed by filtration. Sodium carbonate is then added to remove the excess of silver (and any metals other than alkalies), and the solution is evaporated to dryness and heated until the chlorate is converted into chloride. The presence of the chloride in the residue is ascertained by silver nitrate.

Hydrofluoric Acid and Fluorides

The fluorides of the alkali metals, and of silver, mercury (iron, aluminium, tin), are soluble in water. Those of the alkaline earths, and of lead (copper, zinc, manganese), are insoluble.

Calcium chloride gives with soluble fluorides a transparent gelatinous precipitate of calcium fluoride, CaF_2, partially soluble in hydrochloric acid.

Barium chloride throws down a white precipitate of barium fluoride, BaF_2, partially soluble in HCl.

Silver nitrate gives no precipitate, as silver fluoride is soluble in water (*distinction between a fluoride and the other halides*).

**Liberation of Hydrogen Fluoride.** — Fluorides are

decomposed by strong sulphuric acid, with evolution of gaseous hydrogen fluoride—

$$CaF_2 + H_2SO_4 = CaSO_4 + 2HF$$
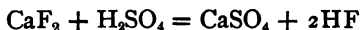
The gas is a colourless, fuming, and highly corrosive compound ; its presence may be detected in the following ways :—

(*a*) **Etching Glass.**—The powdered fluoride is mixed with strong sulphuric acid in a small dish or tray, made of lead (or a platinum capsule). It is covered with a small piece of sheet glass which has been coated on one side with wax, and some marks or words scratched upon the wax. In a few minutes the exposed parts of the glass will have become eaten into or dissolved away by the acid gas ; so that, on removing the wax with a little hot water, the marks or letters will be found to be etched into the glass.

This effect is due to the action of the acid upon silica (and silicates) forming gaseous silicon fluoride—

$$SiO_2 + 4HF = SiF_4 + 2H_2O$$
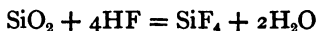
(*b*) **The Decomposition of Silicon Fluoride by Water.**—The powdered fluoride is mixed with sand, and gently warmed in a test-tube with a little strong sulphuric acid ; a glass rod with a drop of water upon the end is lowered into the mouth of the tube. The gas, on coming in contact with the water, is decomposed, and a white deposit of silicic acid is formed upon the rod—

$$3SiF_4 + 3H_2O = 2H_2SiF_6 + H_2SiO_3$$
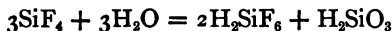
(*c*) **The Formation of Boron Fluoride.**—When a fluoride (finely powdered) is mixed with powdered borax, and the mixture moistened with strong sulphuric acid, gaseous boron fluoride, BF_3, is evolved. The action takes place between the hydrofluoric acid and boric acid, which are disengaged by the action of the sulphuric acid upon the respective compounds—

$$B(HO)_3 + 3HF = 3H_2O + BF_3$$
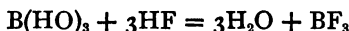
If the mixture be introduced into the edge of a Bunsen flame upon a loop of platinum wire, the flame is tinged a grass-green colour by the escaping boron fluoride.

●

Sulphuretted Hydrogen [1] and Sulphides

Sulphuretted hydrogen is a colourless gas, easily distinguished from all other gases by its unmistakable odour. It is soluble in water, and imparts its own smell to the liquid. The solution, however, is unstable, undergoing oxidation and depositing sulphur. The gas burns with a flame resembling that of burning sulphur, and yields water and sulphur dioxide.

Liberation of sulphuretted hydrogen takes place when certain sulphides (see below) are acted upon by acids. The gas may be recognised (1) by its odour; (2) by its action upon solutions of metallic salts, *e.g.* lead acetate. The reaction is made in a test-tube, and a piece of paper moistened with lead acetate is held over the mouth of the tube. The sulphuretted hydrogen causes a black stain of lead sulphide.

Sulphides of the alkalies and alkaline earths are soluble in water; all other metallic sulphides are insoluble (see Analytical Classification of the Metals).

Soluble sulphides are decomposed by dilute acids (HCl or H_2SO_4), with liberation of sulphuretted hydrogen; in the case of polysulphides, sulphur is also precipitated—

$$K_2S + 2HCl + Aq = 2KCl + H_2S + Aq$$
$$CaS_5 + 2HCl = CaCl_2 + H_2S + 4S$$
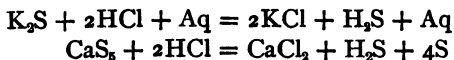
Insoluble Sulphides.—The behaviour of these towards acids has already been considered in detail, in studying the separation of the metals. It may be briefly summarised as follows :—

(*a*) Sulphides decomposed by dilute acids (HCl or H_2SO_4), with liberation of sulphuretted hydrogen : namely, ZnS, MnS, FeS.

(*b*) Sulphides unacted upon by dilute acid, but decomposed by hot strong hydrochloric acid with more or less difficulty : Sb_2S_3, PbS, SnS, NiS, CoS.

(*c*) Sulphides unacted upon by strong hydrochloric acid,

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[1] Sometimes called *hydrosulphuric acid;* the solution of the gas in water has a feeble acid reaction.

but decomposed by *aqua regia*, or by a mixture of hydrochloric acid and potassium chlorate: HgS, As_2S_3.

The sulphides of class (*b*), when treated with hydrochloric acid in the presence of zinc, or, better, of reduced iron, readily evolve sulphuretted hydrogen.

Oxidising agents, *e.g.* nitric acid, convert many of the sulphides into oxides or sulphates, sulphur being first separated and afterwards oxidised into sulphuric acid.

When a sulphide is added (in small quantities at a time) to a fused mixture of sodium carbonate and potassium nitrate in a platinum crucible, the sulphide is immediately oxidised. After the mass has cooled, and been extracted with water, the aqueous liquid may be tested for a *sulphate*. The sulphides of classes (*a*) and (*b*), when fused upon a piece of platinum foil (or, better, silver) with sodium hydroxide, are decomposed, with the formation of sodium sulphide. If a fragment of the fused mass, after cooling, be placed upon a silver coin and moistened with a drop of water, or upon a piece of paper which has been moistened with a solution of lead acetate, in either case a black stain will be produced; silver sulphide on the coin, and lead sulphide upon the paper.

Most sulphides, when heated in a glass tube open at both ends, and held in a slightly inclined position in order to cause an air-current to pass through the tube, are decomposed, and evolve sulphur dioxide.

Sulphuric Acid and Sulphates

Sulphuric acid is an oily, highly corrosive acid liquid. It combines with water with evolution of heat, and is able to abstract the elements of water from many organic compounds. Thus paper, straw, etc., are blackened or charred by the strong acid. This property is made use of in testing for the free acid in the presence of soluble sulphates: a piece of paper is moistened here and there with the solution, and then carefully dried, when it becomes charred where it had been wetted. Or the solution may be mixed with a little white sugar, and evaporated down in a porcelain dish upon a steam-bath, when a charred residue will be left.

Most sulphates are soluble in water. Barium, strontium, calcium, and lead sulphates are insoluble, or nearly so.

Soluble Sulphates.—Barium chloride, $BaCl_2$, gives with sulphuric acid or soluble sulphates, a white precipitate of barium sulphate (see Barium reactions), insoluble in hydrochloric acid. The solutions should be dilute, as barium chloride, being insoluble in strong hydrochloric acid, may otherwise be thrown out of solution; the addition of water dissolves it.

Insoluble sulphates may be decomposed by fusion with sodium carbonate, sodium sulphate being formed. The residue is extracted with water, and the aqueous solution tested with barium chloride after being acidified.

When a sulphate is fused with sodium carbonate (which must be free from sulphates as impurities) upon charcoal in the reducing flame, a sulphide of the alkali metal is obtained. If this be placed upon a piece of paper moistened with acetate of lead, and touched with a drop of dilute hydrochloric acid, sulphuretted hydrogen is liberated, and the lead paper stained black.

[This test is only conclusive evidence of a sulphate when other sulphur compounds are proved to be absent.]

Sulphurous Acids and Sulphites

Sulphurous acid, H_2SO_3, is only known in solution, being produced when sulphur dioxide is passed into water, or when this gas is liberated from combination (as from sulphites) in the presence of water; thus—

(1) In dilute solution—

$$Na_2SO_3 + 2HCl + Aq = 2NaCl + H_2SO_3 + Aq$$

(2) In stronger solution—

$$Na_2SO_3 + 2HCl = 2NaCl + H_2O + SO_2$$
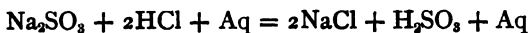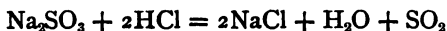
The anhydride, SO_2, is recognised by its characteristic suffocating odour (familiar as "the smell of burning sulphur").

Reducing Action of Sulphurous Acid.—Sulphurous acid easily takes up oxygen, and passes into sulphuric acid, and

some of its most important reactions are those in which it thus acts as a reducing agent. Thus, potassium permanganate is reduced with formation of manganous sulphate—

$$2KMnO_4 + 5H_2SO_3 = K_2SO_4 + 2MnSO_4 + 2H_2SO_4 + 3H_2O$$
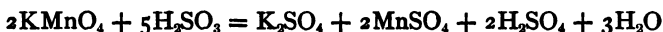
This reaction affords a delicate test for sulphur dioxide. The gas is cautiously decanted (being much heavier than air) into a test-tube containing water slightly tinted with a minute quantity of potassium permanganate. On shaking the gas and water, the pink colour will be destroyed.

Oxidising Action of Sulphurous Acid.—Sulphurous acid is also capable of undergoing reduction, acting therefore towards more powerful reducing agents in the capacity of an *oxidising* substance. Thus, stannous chloride in presence of hydrochloric acid, is oxidised into stannic chloride, the sulphurous acid being reduced to sulphuretted hydrogen. This latter then reacts upon the stannic chloride, with precipitation of stannic sulphide—

(1) $3SnCl_2 + 6HCl + H_2SO_3 = 3SnCl_4 + 3H_2O + H_2S$
(2) $\qquad SnCl_4 + 2H_2S = SnS_2 + 4HCl$

Nascent hydrogen, obtained by the action of hydrochloric acid upon zinc, also reduces sulphurous acid to sulphuretted hydrogen—

$$H_2SO_3 + 3H_2 = 3H_2O + H_2S$$
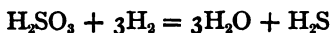
The test may be made by adding a minute trace of sulphurous acid (or a solution of a sulphite) to a mixture of zinc and hydrochloric acid in a test-tube, and applying acetate of lead paper to the mouth of the tube.

Sulphites.—The only sulphites soluble in water are those of the alkali metals. They are all decomposed by dilute acids, with evolution of sulphur dioxide (see above). Oxidising agents convert them into sulphates.

When heated by themselves, most sulphites are converted into sulphides and sulphates—

$$4K_2SO_3 = K_2S + 3K_2SO_4$$

Those of the alkaline earths leave an oxide, and evolve sulphur dioxide—

$$BaSO_3 = BaO + SO_2$$

**Barium chloride** gives a white precipitate of barium sulphite, $BaSO_3$, soluble in dilute HCl (*distinction from* $BaSO_4$).

Lead acetate precipitates white lead sulphite, $PbSO_3$. The salt undergoes no change when boiled (contrast lead thiosulphate).

Silver nitrate gives a white precipitate of silver sulphite, which, on boiling, is converted into black metallic silver—

$$Ag_2SO_3 + H_2O = H_2SO_4 + Ag_2$$
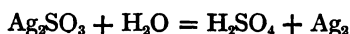
Separation of a Sulphate and Sulphite.—The solution (dilute) is acidulated with hydrochloric acid, and barium chloride added. The precipitated sulphate (insoluble in acid) is removed by filtration. To the solution, which now contains barium chloride and sulphurous acid, an oxidising agent, such as chlorine water, is added, when a precipitate of barium sulphate is again thrown down—

$$BaCl_2 + H_2SO_3 + H_2O + Cl_2 = BaSO_4 + 4HCl$$
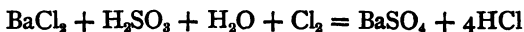
Separation of a Sulphide, Sulphate, and Sulphite.—The sulphide is first separated as an insoluble metallic sulphide by shaking up the solution with a little lead carbonate (or cadmium carbonate). The precipitated sulphide is then removed by filtration. Very small traces of sulphuretted hydrogen will produce a distinct coloration in the white carbonate of lead.

If cadmium carbonate is used the precipitate should be treated with acetic acid, which dissolves the excess of white $CdCO_3$, leaving the yellow CdS.

The sulphate and sulphite in the filtrate are then separated as described above.

Nitric Acid and Nitrates

Nitric acid is a fuming corrosive liquid. It readily dissolves most metals, converting them into nitrates or oxides,

with evolution of oxides of nitrogen, and in some cases with the formation of ammonia.

Nitric acid also oxidises many of the non-metals; thus sulphur, phosphorus, and iodine, are converted respectively into sulphuric, phosphoric, and iodic acids. It is capable also of oxidising indigo, which thereby loses its blue colour, being bleached.

Nitrates are all soluble in water; their recognition, therefore, is based upon the oxidising reactions of which they, or the nitric acid which they yield, are capable.

Reduction by Ferrous Salts.—When ferrous sulphate is brought into contact with a mixture of a nitrate and strong sulphuric acid, the solution assumes a deep brown colour. Three chemical changes go to make up the reaction: (1) the liberation of nitric acid by the action of sulphuric acid upon the nitrate; (2) the reduction of the nitric acid by the ferrous salt, with elimination of nitric oxide; and (3) the absorption of the nitric oxide so formed by a further portion of ferrous salt, forming an unstable brown compound having the composition $NO, 2FeSO_4$. The test is extremely delicate, and is carried out in the following manner: The solution of the nitrate is mixed with about its own·volume of strong sulphuric acid in a test-tube, and the mixture cooled. To this a little ferrous sulphate solution is cautiously added, the tube being held in an inclined position, so that the ferrous sulphate shall float upon the denser liquid already in the tube. Where the two liquids meet, the brown colour will be developed. By a gentle movement of the tube, so as to cause a slight admixture of the liquids at the point where they meet, the brown ring will be still more apparent. The coloured compound is decomposed by heat, with evolution of nitric oxide, hence the necessity for making the test with cold solutions.

Reduction by Sulphurous Acid.—When copper (or mercury) is heated with sulphuric acid in the presence of a nitrate, nitric oxide is evolved, which, in contact with the air, gives red vapours of nitrogen peroxide—

$$3Cu + 4H_2SO_4 + 2KNO_3 = 3CuSO_4 + K_2SO_4 + 4H_2O + 2NO$$

The sulphur dioxide (developed by the action of the acid upon the copper) is oxidised by the nitric acid (simultaneously generated by the action of the acid upon the nitrate) to sulphuric acid; thus—

(1) $$Cu + 2H_2SO_4 = CuSO_4 + 2H_2O + SO_2$$
(2) $$2HNO_3 + 3SO_2 + 2H_2O = 3H_2SO_4 + 2NO$$
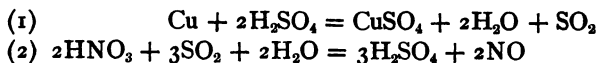
The nitrate is mixed with a little strong sulphuric acid, and a few fragments of copper foil or turnings are introduced. On boiling the mixture, red fumes of nitrogen peroxide, NO_2, will appear in the tube, which will be more easily seen by looking down through the mouth of the tube.

Decomposition by Heat.—Nitrates all undergo decomposition when strongly heated. Nitrates of alkali metals and alkaline earths, when gently heated, are reduced to nitrites, with evolution of oxygen.

Ammonium nitrate passes into water and nitrous oxide. Other nitrates, *e.g.* lead nitrate, leave an oxide of the metal, and give off oxygen and nitrogen peroxide.

When heated with oxidisable substances (carbon, sulphur, etc.) the decomposition is propagated with explosive violence. Thus, when nitrates are heated before the blowpipe on charcoal, deflagration of the charcoal takes place.

Nitrates and **chlorates**, when present together, are examined by being first converted by heat into nitrites and chlorides. If present as salts of metals other than the alkalies, sodium carbonate is added, and the dry mixture heated until the evolution of oxygen is at an end. The residue is extracted with water, and the solution examined for nitrites and chlorides.

If chlorides are originally present as well as nitrates and chlorates, they must be first removed by precipitation with silver sulphate, as explained on p. 90.

Nitrous Acid and Nitrites

The acid is not known in the pure state. Even when liberated in dilute solutions, it speedily breaks up into nitric acid, nitric oxide, and water. Hence when nitrites are decomposed

by acids, nitric oxide is evolved, which, in contact with atmospheric oxygen, passes into the brown gas NO_2; thus—

$$6NaNO_2 + 3H_2SO_4 = 3Na_2SO_4 + 2HNO_3 + 2H_2O + 4NO$$

Nitrites are all soluble in water, but the silver salt is sufficiently difficult of solution to be precipitated, on the addition of silver nitrate, to a (not too dilute) solution of a nitrite.

All nitrites are easily decomposed by *dilute* acids in the cold, with evolution of nitric oxide, as shown in the above equation. If the action takes place in the presence of a ferrous salt, the same brown-coloured compound is produced as in the case of a nitrate. [Nitrites therefore give a "brown ring," when *dilute* sulphuric, or even acetic acid is used (*distinction from nitrates*).]

Oxidation Reactions.—Nitrous acid and nitrites part with oxygen, and are converted into nitric oxide. Thus, in contact with potassium iodide, the latter is oxidised with liberation of iodine—

$$2KI + H_2O + O = 2KHO + I_2$$

Similarly, sulphuretted hydrogen is oxidised by a nitrite in presence of an acid, with precipitation of sulphur—

$$H_2S + 2HNO_2 = 2H_2O + 2NO + S$$
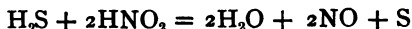
Cobaltous nitrite is oxidised to cobaltic nitrite. When a strong solution of cobalt*ous* chloride mixed with acetic acid is added to a solution of potassium nitrite, a yellow precipitate is obtained, consisting of potassium cobalt*ic* nitrite, $3KNO_2, Co(NO_2)_3$.

Reduction Reactions.—Nitrous acid, by absorption of oxygen, passes into nitric acid; it therefore is capable of reducing other compounds, such as chromates, permanganates, mercurous (but not mercuric) salts.

Detection of Nitrites and Nitrates in the same Solution. —Owing to the ready decomposition of nitrites by dilute acids, they are easily detected in presence of nitrates, either by the liberation of iodine, the oxidation of ferrous salts, or reduction of potassium permanganate. To find a nitrate when nitrites are present is less simple. The dilute solution of the

mixed nitrate and nitrite is acidified with three or four drops of dilute sulphuric acid, and a little ferrous sulphate solution (or a small crystal of the salt) is added. The solution at once becomes dark brown (owing to the absorption, by the ferrous salt, of the nitric oxide liberated from the nitrite). It is then heated (but not allowed to boil), with frequent shaking, when nitric oxide is expelled, and the liquid gradually becomes colourless. The mixture is cooled, and one drop more dilute acid added, and a little more ferrous sulphate. (If all the nitrite present had been decomposed, this addition gives no further coloration.) This solution is now poured carefully on to a small quantity of strong sulphuric acid in a test-tube, so as to float upon the acid, and where the liquids meet a "brown ring" will be formed, due to the nitrate present.

Phosphoric Acid and Phosphates

Three phosphoric acids (each with its series of phosphates) are known, namely, orthophosphoric acid, H_3PO_4; pyrophosphoric acid, $H_4P_2O_7$; and metaphosphoric acid, HPO_3.

Orthophosphoric acid.—The only orthophosphates which are soluble in water are those of the alkali metals.

Silver nitrate gives a *yellow* precipitate with soluble phosphates, of silver phosphate, Ag_3PO_4, which distinguishes ortho from pyro and meta compounds.

Ammonium molybdate gives a yellow precipitate, consisting of ammonium phospho-molybdate (see p. 51). *Pyro* and *meta* phosphates also give the test, because on warming in contact with nitric acid they are transformed into *ortho* salts.

Magnesium sulphate, in presence of NH_4Cl and NH_4HO, gives a white precipitate of ammonium magnesium phosphate, NH_4MgPO_4. (Magnesium reaction, p. 26.)

Action of Heat.—Orthophosphates containing either one or two acidic hydrogen atoms (as HNa_2PO_4 or H_2NaPO_4), or the volatile radical NH_4, yield when heated either *pyro* or *meta* phosphates. Normal phosphates containing only nonvolatile positive radicals are not decomposed.

Pyrophosphoric Acid and Pyrophosphates are produced when orthophosphoric acid or certain orthophosphates are heated.

Boiling with acids retransforms pyrophosphates into orthophosphates.

Only the pyrophosphates of the alkalies are soluble in water.

Silver nitrate gives a white precipitate of silver pyrophosphate, $Ag_4P_2O_7$.

Magnesium sulphate precipitates white magnesium pyrophosphate, $Mg_2P_2O_7$, soluble in excess of magnesium sulphate, and not reprecipitated *in the cold* by ammonia (*distinction from orthophosphates*).

Ammonium molybdate gives no precipitate until the " pyro " acid has been changed to " ortho " by the action of the nitric acid present.

Metaphosphoric Acid and Metaphosphates.—The acid is formed when the " ortho " or " pyro " acids are strongly heated, whereby water is expelled. It is known as *glacial* phosphoric acid—

$$H_3PO_4 = H_2O + HPO_3$$

The reaction is reversible ; for when metaphosphoric acid is dissolved in water, it passes back to the ortho acid—slowly in the cold, quickly when boiled.

Silver nitrate gives a white precipitate of silver metaphosphate, $AgPO_3$.

Magnesium sulphate, in presence of ammonium chloride, gives no precipitate (*distinction from "pyro" and "ortho" acids*).

Albumen (white of egg) is coagulated when shaken up with metaphosphoric acid (or metaphosphates acidified with acetic acid) (*distinction from "pyro" and "ortho" acids, which are without action upon albumen*).

Carbonic Acid and Carbonates

Carbonic Acid, H_2CO_3, is an unstable compound only capable of existence in dilute aqueous solution. It is formed when carbon dioxide is dissolved in water, and has a feeble acid reaction. It is capable of dissolving the normal carbonates of the alkaline earths and of magnesium, forming the so-called " acid " carbonates or " bicarbonates." All normal carbonates are insoluble in water, except those of the alkalies. The " acid " carbonates are all soluble, but on boiling their solutions, they are converted into normal salts, with evolution of carbon dioxide.

All carbonates are decomposed by dilute hydrochloric acid (and by nearly all acids) with effervescence, due to the rapid escape of carbon dioxide. The gas is identified by its action upon lime-water (or baryta-water).

The test is made by adding a few drops of acid to the carbonate in a test-tube, and decanting the evolved (heavy) gas into a second test-tube containing a little lime-water, $Ca(HO)_2$. On shaking the lime-water with the gas, the liquid becomes milky, owing to the precipitation of calcium carbonate.[1]

When strongly heated, the normal carbonates of the alkali metals (not ammonium) remain unchanged. Those of the alkaline earths are converted at a high temperature into oxides, with evolution of carbon dioxide (illustrated in the process of lime-burning). All other carbonates are more readily decomposed by heat.

Silicic Acid and Silicates

Silicic acid, H_2SiO_3, is obtained, when soluble silicates are decomposed by acids, as a white gelatinous substance, slightly soluble in water, and still a little more soluble in acids—

$$Na_2SiO_3 + 2HCl = H_2SiO_3 + 2NaCl$$

Silicic acid is also precipitated from a solution of an alkali silicate by the addition of ammonium carbonate (ammonia does not cause any precipitate)—

$$Na_2SiO_3 + (NH_4)_2CO_3 = Na_2CO_3 + 2NH_3 + H_2SiO_3$$

Silicic acid is a very feeble acid, and when heated to 130° C. it parts with a molecule of water, and is converted into

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[1] The only other gas which gives a white precipitate with lime-water is sulphur dioxide. This is easily distinguished from carbon dioxide by its smell. If the two gases are present together, they may be passed through a little dilute potassium permanganate solution. The sulphur dioxide is absorbed (being oxidised by the permanganate into sulphuric acid), and the carbon dioxide passes on, and can be detected by means of lime-water. If the passage of the gases through the permanganate be continued for a few minutes, the colour of the solution becomes entirely destroyed ; and the liquid may then be tested for sulphuric acid in the usual way.

silicon dioxide (*silica*), SiO_2, a compound which is insoluble in water and in acids.[1]

Silica, SiO_2, occurs in a more or less pure state in nature, in the form of *quartz, flint, agate, sand*, etc. When prepared artificially by heating the hydrated compound, it is a white amorphous powder. It is extremely stable, and capable of standing a very high temperature. It is insoluble in water and all acids except hydrofluoric acid. It dissolves in caustic alkalies; and, when in the amorphous state, in boiling carbonates of the alkalies, yielding in all cases the soluble alkali silicates.

The only silicates which are soluble in water are the alkali silicates (known as *water glass*, or *soluble glass*).

The presence of silica is detected by means of its behaviour when heated with microcosmic salt. A clear bead of this salt is made upon a loop of platinum wire, and a few small particles of the powdered silicate are heated in it. The metallic oxides are dissolved by the fused microcosmic salt, but not the silicon dioxide, particles of which (the skeletonic remains of the mineral) remain floating about in the molten bead.

Silica may also be detected by the formation of silicon fluoride when the compound is acted upon by hydrofluoric acid. The test is made as described under hydrofluoric acid (p. 91).[2] In this case, however, the drop of water which is suspended in the gas in order to detect the silicon fluoride, should be held on a loop of platinum wire, as the action of the hydrofluoric acid upon the glass rod might be mistaken for a deposition of silica.

Insoluble silicates may be classified for analytical purposes into (1) those which are decomposed by acids (other than hydrofluoric acid); and (2) those which are unattacked, which comprises by far the larger class.

(1) **Silicates which are decomposed by acid** may have their silica removed by treatment with hydrochloric acid. The mineral, in as finely powdered a condition as possible, is

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[1] Silicic acid is sometimes spoken of as *soluble silica*, and silicon dioxide as *insoluble silica*.

[2] Except that in this case the test must not be made in glass vessels (which are themselves silicates) but in a lead or platinum capsule.

digested with strong hydrochloric acid at a gentle heat, when gelatinous silicic acid separates, and the powdered mineral gradually dissolves. The mixture is next evaporated to dryness (preferably on a steambath), and then gently heated over a flame for a short time in order to ensure the entire conversion of the silicic acid into silica. The residue is treated with a small quantity of strong hydrochloric acid, water is added, and the solution containing the metals present as chlorides is separated by filtration from the insoluble residue of silica.

(2) **Silicates which are unattacked by acids** are decomposed by fusion with alkali carbonates. The finely powdered silicate is mixed with several times its weight of *fusion mixture*, and the mixture heated in a platinum crucible. The fusion is continued until effervescence ceases, the temperature being raised towards the end of the operation. The residue, after cooling, is extracted with water, which dissolves the alkali silicate (and excess of carbonate), leaving the metallic oxide (or carbonate). Hydrochloric acid is then gradually added, which causes the precipitation of silicic acid, and at the same time dissolves the metallic oxides. The mixture is then evaporated, and treated in the manner described above.

Fusion with alkali carbonates is obviously inadmissible in the case of natural silicates which are suspected of containing the alkali metals, and which are insoluble in hydrochloric acid. In this case, one of the following plans may be employed :—

(*a*) **Heating with Ammonium Chloride and Calcium Carbonate.**—A small quantity of the powdered silicate is mixed with about an equal weight of ammonium chloride and about eight times its weight of calcium carbonate (precipitated), and the mixture gently heated in a platinum crucible until no more fumes of ammonium chloride are given off. It is then strongly heated with the blowpipe for about fifteen minutes, after which the mass is treated with water. The alkalies, in the form of chlorides, together with a small quantity of calcium chloride, pass into solution, and are separated by filtration. The calcium is removed by precipitation with ammonium carbonate, and the filtrate evaporated and examined for alkalies.

(*b*) **Decomposing the Silicate with Hydrofluoric Acid.—**

This may be accomplished by treating the powdered mineral with aqueous hydrofluoric acid in a platinum crucible, gently evaporating the liquid (in a draught cupboard) to dryness, adding fresh acid and evaporating again, continuing the operation until the residue is entirely soluble in hydrochloric acid.

Boric Acid and Borates

Boric acid, H_3BO_3, is a white crystalline solid, sparingly soluble in cold, but more readily soluble in hot, water. It is deposited from its solutions in the form of pearly white scales.

It is also soluble in alcohol, and when either the aqueous or alcoholic solution is boiled, the acid vaporises along with the solvent.

When heated, boric acid (ortho), H_3BO_3, loses water, passing first into metaboric acid, $H_2B_2O_4$, and finally into pyroboric acid, $H_2B_4O_7$.

The borates of the alkalies are readily soluble in water; most other borates are insoluble. A few (*e.g.* magnesium borate) are difficultly soluble. The most familiar salts are those of pyroboric acid, *e.g.* ordinary borax, $Na_2B_4O_7$.

The insoluble borates obtained by precipitation are not characteristic, and are not used in analysis for the detection of borates.

All borates are decomposed by mineral acids, with liberation of orthoboric acid; thus—

$$Na_2B_4O_7 + 2HCl + 5H_2O = 2NaCl + 4H_3BO_3$$

Reaction with Turmeric.—Boric acid produces upon turmeric paper a characteristic red-brown stain. This coloration is distinguished from that produced by alkalies (which it closely resembles in appearance) by the fact that when touched with an alkali the brown colour is changed to a greenish-black, but is restored to its original tint by dilute acids (HCl or H_2SO_4). The borate is moistened with hydrochloric or sulphuric acid in order to liberate the boric acid, and a drop or two of the liquid is poured upon the turmeric paper.

Flame Reactions.—Volatile boron compounds impart a characteristic green colour to the flame; thus, when an alcoholic

solution of boric acid is boiled, and the alcohol vapour inflamed, the green colour due to the volatilised boric acid is apparent. The test is made in the following manner :—

The borate (borax) is moistened with a little strong sulphuric acid in a test-tube or small flask, and alcohol is added. The test-tube is closed with a cork carrying a short straight glass tube. The contents of the tube are then heated, and as the alcohol boils off it is inflamed at the exit tube, when the green colour of the flame is observed.

A small quantity of the powdered borate (or boric acid) is mixed with about its own weight of powdered calcium fluoride, and the mixture moistened with one or two drops of strong sulphuric acid. A little of the paste is introduced into a Bunsen flame upon a loop of platinum wire. By the action of the acid upon the fluoride, hydrofluoric acid is formed; and this in the presence of the borate gives boron fluoride, BF_3, which causes a green coloration of the flame. The presence of copper salts masks the reaction.

Permanganic Acid and Permanganates

The acid is not met with in analysis. The permanganates are all soluble in water, therefore no precipitates by double decomposition are produced with these salts. Their chief properties are their oxidising powers, which have been already described under the reactions for manganese (p. 44).

Arsenates and **Chromates** have already been treated under Arsenic (p. 64) and Chromium (p. 35).

CHAPTER X

PRELIMINARY EXAMINATION FOR METALLIC RADICALS

A. When the Substance under Examination is a Liquid.—
Before proceeding to the group separation, the liquid should be
carefully tested with litmus paper, in order to ascertain whether
it is neutral, acid, or alkaline.

(1) *If neutral*, the liquid might be simply water. To
ascertain whether or not it contains anything in solution, a few
drops should be placed upon a watch-glass and carefully
evaporated to dryness. If there is no residue left in the watch-
glass, it contained no salts in solution, and was therefore simply
water.

(2) *If acid*, the solution may contain either a free acid, or
salts possessing an acid reaction. [Either certain normal salts,
e.g. copper sulphate, alum, etc., or certain "acid" salts, as
hydrogen sodium sulphate.]

(3) *If alkaline*, the liquid may contain either free alkali, or
salts having an alkaline reaction.

B. When the substance is a solid, it should be critically
examined, in order, if possible, to gain any information from
its general physical properties which may help to identify it.
If crystalline, the colour, shape, etc., of the crystals should be
noted. If powdered, it may be examined with a pocket-lens, in
order to discover whether or not it is homogeneous; *i.e.*
whether it is a single compound, or a mixture of more than one.

The substance should then be subjected to the following
general tests [1] :—

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[1] Every smallest detail of these preliminary tests should be carefully
and systematically noted down, whether the interpretation of the observa-
tion is obvious to the student or not.

I. **The Flame Reaction.**—A small quantity of the substance is introduced into the edge of the Bunsen flame (first in the cooler region near the base of the flame, and afterwards in the hotter parts near the top of the interior cone) upon a loop of clean platinum wire. The flame is coloured—

Intense yellow, by compounds of *sodium*.

Violet, appearing red through the potassioscope, *potassium*.

Crimson, compounds of *strontium*.

Orange red   „   *calcium*.

Pale green   „   *barium*.

Green   „   *copper, boric acid*.

Obviously the presence of one of these substances may modify or mask the colour reaction due to another.

II. **The Borax Bead.**—A minute particle of the substance is heated in a borax bead in the blowpipe flame, both inner and outer flame. The bead is coloured—

Blue (both outer and inner flame) indicates *cobalt*.

Brown (outer), *grey* (inner), compounds of *nickel*.

Violet (outer), colourless (inner), compounds of *manganese* (also mixture of Co and Ni).

Brown, cooling to yellow (outer), *green* (inner), *iron*.

Green (outer and inner), compounds of *chromium*.

Green, cooling to bluish (outer), *red* (outer), *copper*.

Here, as with the flame test, one substance modifies or masks the reaction due to another.

[Should this test lead to the suspicion that either manganese or chromium is present, it should be followed up by the fusion of a portion of the substance with sodium carbonate and nitre upon platinum foil. See Manganese and Chromium reactions.]

III. **Blowpipe Reactions upon Charcoal.**—(*a*) *When heated alone.*—A considerable amount of information may be obtained by heating a little of the substance by itself upon charcoal.

(1) *If it melts and is absorbed into the charcoal*, it points to the substance consisting of salts of the alkalies. [Chlorates and nitrates cause vivid combustion of the charcoal.]

(2) *If a white infusible residue is obtained*, the substance may consist of oxides (or salts which yield oxides when

heated) of the *alkaline earth metals, alumina, zinc* (ZnO yellow while hot, white when cold), or of silica. [If the residue, when placed upon a piece of tumeric or litmus paper and moistened with water, shows an alkaline reaction, it will contain one of the alkaline earth metals. Silica may be specially tested for by the bead of microcosmic salt.]

(3) *If a coloured residue is left*, it points to one of the metals already indicated by the borax-bead test.

(4) *If reduction takes place*, resulting in the formation of fumes and an incrustation upon the charcoal, without indication of a metallic bead, it points to the presence of compounds of very volatile metals, as *arsenic* (white incrustation accompanied by garlic odour), *cadmium* (red-brown incrustation), *zinc* (incrustation yellow when hot, and forming very close to the substance). Such a volatile compound as *ammonium chloride* gives white fumes and an incrustation (the latter being formed at a considerable distance from the heated spot). In this case the blowpipe flame appears of a yellow-ochre colour as it impinges upon the ammonium salt.

(*b*) *When heated with Reducing Agents.*—When the substance is mixed with sodium carbonate and potassium cyanide, and heated upon charcoal in the reducing flame, compounds of *copper* and *silver* are reduced to the metallic state without giving any incrustation upon the charcoal ; while compounds of *antimony, bismuth, tin*, and *lead* give metallic beads accompanied by incrustations (for the characteristics of the incrustations and the metals, see Special relations of each).

IV. **The Action of Heat.**—The behaviour of a substance when heated alone in a dry narrow tube closed at one end (a small test-tube), will generally afford important information respecting its composition.

A. **If the substance simply melts, and solidifies on cooling**, without giving off any gases or vapours, a large number of compounds are obviously at once excluded. In this case the substance may consist of salts of the alkalies or the alkaline earth metals ; a few white salts of the heavy metals, *e.g.* silver chloride ; or a few coloured salts, *e.g.* lead chromate.

B. **If water is given off**, collecting in drops upon the upper

part of the tube, it may be due (1) to hygroscopic [1] moisture (in this case the amount will probably be small), (2) to the decomposition of metallic hydroxides, or (3) to water of crystallisation. [Substances containing much water of crystallisation, when heated, often melt *twice*—first in the water of crystallisation, and as this is expelled they resolidify, but on the application of a stronger heat they once more undergo fusion.]

The water should be carefully tested by introducing a small strip of litmus paper.

Alkalinity would indicate ammonium compounds (*e.g.* $(NH_4)_2MgPO_4$, $HNa(NH_4)PO_4$, etc.).

Acidity might be due to the decomposition of certain acid salts, either alone or by interaction with other salts (*e.g.* hydrogen potassium sulphate, when heated, is converted into the normal salt and sulphuric acid, and if present along with a salt containing water of crystallisation, the water would become acid ; or if mixed with sodium chloride or nitrate, hydrochloric acid or nitric acid would be evolved by double decomposition).

C. If the substance changes colour—

(1) From white to yellow, indicates oxide of zinc, tin, bismuth ;

(2) From yellow to brown (fusing at a red heat), oxide of lead.

Most coloured oxides become much darker when heated (*e.g.* HgO, Fe_2O_3).

D. If gases or vapours are evolved, they must be identified by special tests.

(1) Oxygen and nitrous oxide (re-ignition of glowing splint of wood). The former from chlorates, nitrates, or peroxides ; the latter from ammonium nitrate, or salts which by double decomposition give ammonium nitrate.

(2) Nitrogen (extinguishes flame, and gives no reaction with lime-water), from ammonium nitrite or chromate, or from mixtures which yield these salts by double decomposition.

(3) Chlorine, bromine, and iodine (recognised by colour,

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[1] That is moisture due to the substance being " damp "—mechanically adhering moisture. Almost all powders attract a little moisture in this way from the atmosphere.

smell, etc.), evolved from certain halogen compounds when heated alone, or in admixture with acid salts and peroxides (*e.g.* a mixture containing such compounds as NaCl, HKSO₄, and MnO₂, when heated, evolves chlorine).

(4) Carbon dioxide (action on lime-water), from most carbonates other than the normal salts of the alkalies.

(5) Sulphur dioxide (characteristic odour), from certain sulphites and sulphates.

(6) Ammonia (odour, and action on test-paper), from ammonium salts.

(7) Sulphuretted hydrogen (odour, and action on paper moistened with lead acetate), from the decomposition of hydrated metallic sulphides.

(8) Nitrogen peroxide, from the decomposition of nitrates of heavy metals.

E. If a sublimate is produced, it indicates such volatile solids as the following :—

(1) Giving a white sublimate—ammonium haloid salts, arsenious oxide, mercuric chloride, mercurous chloride (yellowish white hot, white on cooling).

(2) Giving a coloured sublimate—mercuric iodide (red and yellow), arsenious sulphide (yellow).

(3) Giving a black metallic-looking sublimate—iodine (violet vapours), mercuric sulphide (red streaks if rubbed with a glass rod), metallic mercury (runs into liquid globules when rubbed with a glass rod), metallic arsenic (garlic smell). [If this test leaves it doubtful whether arsenical or mercurial compounds are present, a little of the substance should be mixed with sodium carbonate and heated in a dry tube. If mercurial, the sublimate consists of minute globules.]

Ammoniacal compounds may be at once tested for by heating a portion of the substance with a little sodium hydroxide, when ammonia is evolved.

F. If no change takes place, it will be evident from the foregoing that the number of substances which can possibly be present is extremely limited ; and if in addition the compound is *white*, the range of probable substances is still further narrowed down to the oxides of a few of the metals, such as the alkaline earths, alumina, silica, etc.

To obtain a Solution of the Solid Substance.—(1) **In Water.**—A small quantity of the substance, in a finely powdered condition, is treated with water in a large test-tube, and the mixture boiled for a few moments.

If the substance does not appear to dissolve, it is either wholly or partly insoluble in water. To ascertain whether any of it has dissolved, the mixture should be allowed to settle, and a few drops of the clear liquid evaporated to dryness upon a watch-glass. If a residue is obtained on evaporation (thus showing that partial solution in water has taken place), the aqueous liquid is decanted off, and the insoluble portion again boiled with water and filtered.

(2) **In Acids.**—The portion insoluble in water is then treated with dilute hydrochloric acid and boiled. If it does not entirely dissolve, the dilute acid is decanted off into another test-tube, and strong hydrochloric acid substituted, the mixture being submitted to prolonged boiling, if necessary. If the substance wholly dissolves, the two acid solutions may be mixed together.

If, on adding a few drops of the aqueous extract to a small portion of the acid solution, no precipitation takes place, the main portions of the two solutions may be mixed together. On the other hand, if the two extracts contain compounds which will interact with the formation of an insoluble precipitate, they must be examined separately.

If the substance is not entirely dissolved by strong hydrochloric acid, it may consist of one of the few compounds which are only dissolved by *aqua regia*.[1] The residue is therefore treated with a small quantity of mixed nitric and hydrochloric acids, and boiled. The solution should be evaporated down in a porcelain dish until only a small bulk remains, in order to expel as much acid as possible, and then diluted with water; this solution may then be mixed with the hydrochloric acid extract.

(3) **Treatment of Substances insoluble in Water or in**

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[1] Such as sulphides of nickel, cobalt, mercury. The presence of these should have been indicated by the preliminary tests. The use of *aqua regia* should only be resorted to when absolutely necessary.

Acids.—The number of compounds insoluble in water and acids is very limited. Of commonly occurring substances, the following may be present :—

(*a*) Sulphates of barium, calcium, strontium, and lead (the three last named being sufficiently soluble to be detected in the aqueous extract).

(*b*) Silica, and many natural silicates.

(*c*) Fluor spar, and other natural fluorides.

(*d*) Silver chloride.

(*e*) Oxides of aluminium and chromium (which have been strongly heated). Native stannic oxide (*tinstone*).

(*f*) A few arsenates and phosphates.

These insoluble substances are converted into soluble compounds by fusion with alkali carbonates. The insoluble residue (in the absence of lead and silver) is dried, and mixed with about four times its weight of fusion mixture and a little potassium nitrate, and fused in a platinum crucible[1] until all effervescence is at an end. The crucible is then allowed to cool.

The fused mass is then boiled with water until nothing further dissolves, and the solution filtered.

The *aqueous solution* is examined for such acid radicals as in the nature of the case could be present—namely, sulphuric, silicic, hydrofluoric, chromic, arsenic, phosphoric, hydrochloric.[2]

The *residue*, after being thoroughly washed with hot water, until the wash-water is no longer alkaline, is dissolved in hydrochloric acid, and the solution examined for such metallic radicals as can be present.

[1] If lead or silver is present (ascertained during the preliminary examination), a platinum crucible must not be used.

[2] The fusion-mixture must obviously be free from sulphates, chlorides, etc., or tests for these acids are of no value.

CHAPTER XI

PRELIMINARY EXAMINATION FOR ACID RADICALS

(1) **By the Action of Dilute Acids.**—Dilute HCl or H_2SO_4 is added to the substance, and the mixture *gently* warmed. Effervescence may take place owing to the escape of—

CO_2 from *carbonates.* Apply lime-water test.

SO_2 „ *sulphites.* Recognised by smell. If along with CO_2, apply permanganate test.

NO „ *nitrites.* Shows itself as brown vapour, NO_2.

H_2S „ *sulphides.* Recognised by smell, and acetate of lead paper.

Cl (when the acid used is HCl, and the liquid boiled) from *chlorates, chromates, nitrates, peroxides.*

(2) **By the Action of Strong Sulphuric Acid.**—On gently warming the solid with a little strong H_2SO_4 in a test-tube, the following gases or vapours may be evolved : [1]—

HCl from *chlorides.*

HF „ *fluorides* (in contact with the glass test-tube, SiF_4 will be evolved).

HNO_3 (with more or less brown fumes) from *nitrates.*

Cl from a *chloride,* in presence of *peroxides* or *chromates.*

ClO_2 „ *chlorate* (a deep-yellow gas, the mixture detonates).

Br „ *bromide* (brown vapour, with generally sufficient HBr to fume in moist air).

CrO_2Cl_2 from a mixed *chloride* and *chromate.* (Brown vapour resembling Br in colour.)

I from an *iodide* (violet vapour, accompanied by fumes due to HI).

[1] Care must be taken not to heat the mixture so strongly as to volatilise the sulphuric acid, the acid fumes from which might be mistaken for other gases.

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CLASSIFICATION AND SYSTEMATIC DETECTION OF ACID RADICALS

The acids are classified into three main groups based upon the solubility of their barium and silver salts.

Group I.—Acids whose barium salts are precipitated from *neutral* solutions by barium chloride.

(*a*) Whose barium salts are insoluble in dilute hydrochloric acid—

$$\text{Sulphuric acid, } H_2SO_4$$

(*b*) Whose barium salts are soluble in hydrochloric acid—

Carbonic acid,	H_2CO_3	Phosphoric acid,	H_3PO_4
Sulphurous ,,	H_2SO_3	Boric ,,	H_3BO_3
Silicic ,,	H_2SiO_3	Hydrofluoric ,,	HF
Chromic ,,	H_2CrO_4		

Group II.—Acids whose silver salts are precipitated by silver nitrate from solutions acidified with nitric acid—

Hydrochloric acid,	HCl	Hydriodic acid,	HI
Hydrobromic ,,	HBr	Sulphuretted hydrogen,	H_2S

Group III.—Acids whose barium salts are soluble in water, and whose silver salts are not precipitated in a nitric acid solution, namely—

Nitric acid,	HNO_3	Chloric acid,	$HClO_3$
Nitrous ,,	HNO_2		

As already mentioned (p. 83), these general reagents, barium chloride and silver nitrate, are not employed to effect the *separation* of groups of acids, but rather as indicators of the presence or absence of entire groups.

In most cases, each acid is individually tested for in separate portions of specially prepared solutions (see below).

The examination for acids should be made *after* the metals have been detected, for two reasons: firstly, because during the course of the systematic examination for the metals, the presence or absence of quite a number of acids will be incidentally ascertained; and secondly, because a knowledge of

what metals are present will be a guide to the student in deciding what acids *may* and what *cannot possibly* be present.

As stated above, several acids will be detected during the examination for metals; thus—*on acidifying with hydrochloric acid* and gently warming (for separation of Group I.), the presence of *carbonates, sulphites, sulphides,* or *nitrites* will be indicated. (See preliminary tests.)

On treatment with sulphuretted hydrogen, in the separation of the metals of Group II., indications will have been obtained of the presence of *chromates* and *iodates :* the former by the change of colour from orange to green, with simultaneous precipitation of sulphur ; the latter by the elimination of iodine, which gives a dark brown colour to the solution, the colour gradually disappearing as the excess of sulphuretted hydrogen converts the iodine into hydriodic acid.

On the preparation of the solution for separating the metals of Group III., the presence or absence of *phosphates* and *silicates* will have been ascertained.

Besides these, indications of the presence of several acids will have been obtained during the preliminary examination for metallic radicals.

Preparation of the Solution for the Detection of Acids. —Before testing for the acids, it is advisable (in many cases it is *necessary*) that they should be present in the solution as salts of the alkalies (or alkaline earths); that is to say, the metals with which the various acids are united in the substance under analysis should be exchanged, by double decomposition, for an alkali metal; for the reason that the presence of these other metals would in many cases mask the reactions by which the acids are to be detected. To accomplish this, the solution is boiled,[1] and sodium carbonate added in quantity slightly in excess of that required to effect complete precipitation. The mixture is then filtered, and the acids, now present as their sodium salts, are detected in the solution.[2]

[1] In cases where the substance under analysis is insoluble, the product obtained by fusion with sodium carbonate is extracted with water, and the solution so obtained is employed for the detection of the acids (see p. 113).

[2] This method for separating the metals from their acids is not, ever, of universal application. Thus, in the case of many of the phosphates

GENERAL TESTS.—(1) A small portion of this solution is carefully neutralised by first adding dilute nitric acid drop by drop (the mixture being heated to expel carbon dioxide), until the liquid is *just acid*, and then adding a drop or two of dilute ammonia.

This neutral solution is then tested by the addition of barium chloride. If no precipitate is obtained, the acids of Group I. are absent. If a precipitate is formed which re-dissolves on the addition of hydrochloric acid, sulphuric acid is excluded.

(2) A second small portion of the solution is acidified with nitric acid, and tested with silver nitrate. A negative result proves the absence of the acids of Group II.

If these general tests show that acids of both Groups I. and II. are present, special tests must then be applied in separate portions of the solution, for such acids as, from information already gained, are considered likely to be in the substance under analysis, and which have not been definitely discovered during the course of the examination. The tests may be made in accordance with the following outline scheme, in which most of those acids which must certainly have been detected in the earlier stages are not again mentioned.

A. *In portions of the solution acidulated with hydrochloric acid.*

Sulphuric Acid.—Barium chloride precipitates white barium sulphate: not dissolved by the addition of strong hydrochloric acid, and boiling the liquid.

Silicic Acid.—Ammonium carbonate (but not ammonia) precipitates silicic acid.

Arsenic Acid.—If arsenic has been found among the metals and its state of oxidation (*i.e.* whether present as an arsenite or arsenate) has not been determined, the following test may be applied: Ammonium chloride, ammonia, and magnesium

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held in solution by acids, the action of the sodium carbonate is to cause the precipitation of the *phosphates themselves ;* in such instances, therefore, the acid is not found in the solution. Since, however, phosphoric acid will have been discovered during the examination for the metals, this fact is of little consequence.

sulphate are added—a white precipitate may be due to either a phosphate or arsenate. If phosphoric acid has been proved to be absent (by the molybdate reaction), it must be the arsenate. In either case it should be filtered, and after being washed free from ammonium chloride, it is dissolved in a little nitric acid, and silver nitrate added (or a drop or two of silver nitrate may be poured upon the washed precipitate in the funnel). A brown precipitate indicates an arsenate.

B. *In portions acidulated with nitric acid.*

Hydrochloric.—Silver nitrate gives a white precipitate.

Hydrobromic and Hydriodic Acids.—Silver nitrate gives a yellowish precipitate.

(For the methods of discriminating between these, see p. 89.)

C. *In portions acidulated with acetic acid.*

Hydrofluoric Acid.—Calcium sulphate or chloride precipitates calcium fluoride: only slightly soluble in hydrochloric acid.

(Chromic, phosphoric, and arsenic acids may also be looked for in portions of this solution. These acids, however, will have been detected at an earlier stage of the analysis.)

CHAPTER XII

SIMPLE VOLUMETRIC DETERMINATIONS

WHEN sulphuric acid is added to sodium hydroxide we know that the acid gradually neutralises the alkali, and that a point is reached when the solution shows neither acid nor alkaline properties—it is, in fact, *neutral.* We indicate this action by the equation—

$$H_2SO_4 + 2NaHO = Na_2SO_4 + 2H_2O$$
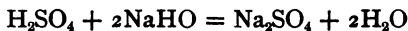
We know also that this means that $2 + 32 + 64 = 98$ grams of sulphuric acid are capable of neutralising $2 (23 + 1 + 16) = 80$ grams of sodium hydroxide. If therefore we have a solution of sulphuric acid, the strength of which is such that 1 litre contains 98 grams of H_2SO_4; and suppose, further, that it took exactly 100 c.c. of this acid to neutralise a given solution of caustic soda of unknown strength, we should then have determined the actual weight of sodium hydroxide present in the latter solution to be 8·0 grams. Or, again, if the alkali were in the solid state, a weighed quantity of it might be dissolved in water so as to make a known volume of solution, and the volume of acid necessary to exactly neutralise either the whole or a measured portion of it would enable us to find the percentage of alkali in the solid. By this operation of *measuring the volume* of acid, we thus *determine the weight* of caustic soda present.

The reagents of known strength (the acid in the above illustration) which are used in volumetric analysis are called *standard solutions.*

Weighing.—It will be evident that *Weighing* must be at the root of all volumetric processes, for not only must the materials to be analysed be accurately weighed, but the standard solutions themselves can only be prepared (in most cases) by exact weighings of the materials contained in them.

In order to obtain the weight of a substance with sufficient

exactness for these volumetric purposes, a moderately delicate balance must be used, and the operations conducted with some care. The object to be weighed is placed upon the left scale-pan, and a weight, which by a guess is judged to be rather greater than that of the object, is placed upon the opposite scale by means of the forceps[1]—the balance being at rest.[2] The beam is then liberated from its supports by means of the lever. Suppose the 20-gram weight had been taken, and it is found to be too little, the beam is brought to rest, and a 10-gram weight added. If this is too much, it is returned to its place in the weight-box, and the 5-gram substituted. If this is too little, the 2-gram is added; if still too little, the 1-gram is added; and should this be too much, the weight then lies between 27 and 28 grams. The same systematic process is continued with the subdivisions of the gram, until the object is so counterpoised that, as the beam gently swings, the pointer oscillates along the scale to practically the same distance in both directions. The result of a weighing operation should be recorded *before removing the weighed object from the scale.* The value of the weights should first be read off *from the empty spaces in the weight-box,*[3] and the result then checked as the weights are returned in order from the highest to the lowest to their places in the box.

With the exception of pieces of metal, alloys, etc., substances to be weighed must never be placed directly on the balance, but must be contained in a suitable vessel. When taking a weighed quantity of a substance for analysis it is usual to obtain its weight by *difference,* in one of two ways : (1) some suitable vessel, such as a watch-glass or porcelain crucible, is weighed—being perfectly dry and clean—and then a sufficient quantity of the substance is placed in it, and the whole re-

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[1] None of the weights, or the moving parts of the balance, must be handled with the fingers.

[2] The balance must always be brought to rest before placing anything upon, or removing anything from, the pans.

[3] This implies two things, (1) that the box of weights is complete, and (2) that the student tidily returns each weight to its proper place which has been taken out but is not in actual use upon the balance when the weighing is completed.

weighed; or (2) the substance contained in a light, thin glass bottle (*a weighing bottle*) is weighed, and a sufficient quantity of it is then carefully tipped out into a beaker or flask, as the case may be, and the bottle and remaining contents re-weighed. In either case the difference between the two weighings is the weight of the substance employed.

Standard Solutions are usually made of such a strength that the quantities of the positive or negative constituents, or of what may be called the *active* constituents of the compounds in the solutions shall bear the same relation to each other as the numbers which express their *chemical equivalents ;* that is to say, equal volumes of the different solutions will contain *equivalent proportions* of the effective constituent of the substance in solution. For example, standard solutions of NaCl and AgNO₃ will be of such strengths that whatever volume of the first contains 35·5 grams of chlorine, the same volume of the other shall contain 108 grams of silver ; or, again, standard solutions of HCl, NaHO, and Na₂CO₃ will be of such strengths that whatever volume of the first contains 1 gram of hydrogen, the same volume of the others shall each contain 23 grams of sodium.

Normal Standard Solutions are solutions of such a strength that the particular volume which contains 1 gram of hydrogen, 23 grams of sodium, 35·5 grams of chlorine, etc., is 1 litre. A normal solution of HCl, to contain 1 gram of hydrogen in the litre, must obviously contain $1 + 35·5 = 36·5$ grams of HCl per litre. Similarly, normal NaHO, to contain 23 grams of sodium to the litre, must contain $23 + 1 + 16 = 40$ grams NaHO per litre ; while a solution of Na₂CO₃, to contain 23 grams of sodium to the litre, must obviously contain $\dfrac{46 + 12 + 48}{2}$ $= 53$ grams of the salt in the same volume, and normal H₂SO₄ must contain $\dfrac{2 + 32 + 64}{2} = 49$ grams of that acid.

In some cases it is only a *portion* of some particular radical or element present in the solution which takes an active part in the particular chemical reactions for which the solution is used. For example, potassium dichromate, K₂Cr₂O₇, is employed as an oxidising agent, but only three out of the seven oxygen

atoms in the salts are available for this purpose; the compound may be regarded as breaking down into K_2O, Cr_2O_3, $3O$. A normal solution of this salt, therefore, when it is to be employed for oxidation reactions, must contain 8 grams of available oxygen (*i.e.* the weight of oxygen equivalent to 1 gram of hydrogen); it must therefore contain $(K_2O)\dfrac{94}{6} + (Cr_2O_3)\dfrac{152\cdot8}{6}$

$+ (3O)\dfrac{48}{6} = 49\cdot13$ grams of the dichromate in 1 litre.

If a standard solution of potassium dichromate were required for precipitating an insoluble chromate by double decompositon such as lead chromate, or barium chromate, then the *normal* solution would have quite a different strength. In this case the reaction would be merely the replacement of potassium by another metallic radical, and the normal solution would be required to contain 39 grams of K to the litre; therefore $(K_2)\dfrac{78}{2} + (Cr_2)\dfrac{104\cdot8}{2} + (O_7)\dfrac{112}{2} = 147\cdot4$ grams of

potassium dichromate would be the weight of salt in 1 litre.

Standard solutions of *one-half, one-tenth,* and *one-hundredth* of the strength of a normal solution are called respectively *semi-normal, deci-normal,* and *centi-normal* solutions. In preparing standard solutions the weighed quantity of salt is not added to and dissolved in the measured volume of water, but it is first dissolved in a moderate quantity of water, and the solution then made up to the exact volume required by adding water. This operation is carried out in a flask capable of holding either 1 litre or $\frac{1}{2}$ litre when filled to a graduation mark upon the neck.

Pipettes are practically glass tubes with a bulb or enlargement upon them, and drawn to a point at one end. Fig. 11 shows two forms of pipette. Like the flasks, they have one graduation mark upon the stem, and are made of various capacities such as 5, 10, 15, 20, 50, and 100 c.c. A pipette is filled by sucking the liquid up until it is somewhat higher than the graduation mark (avoiding sucking it up into the mouth), and then quickly covering the upper end with the finger. Then, by slightly releasing the pressure of the finger, the liquid is allowed to drip slowly out until the level is exactly opposite the graduation mark. When

the contents of the pipette are allowed to flow out, the drop or two which remain in the pointed end may be blown out.

Burettes.—The burette is a long straight glass tube, one end of which is drawn down and terminated by a glass stop-cock, or connected to a jet by means of a caoutchouc tube which can be closed by means
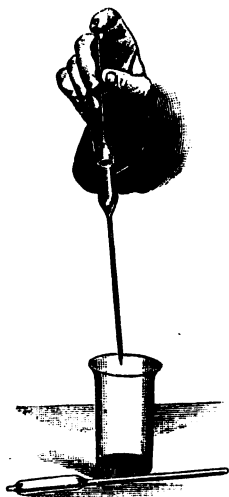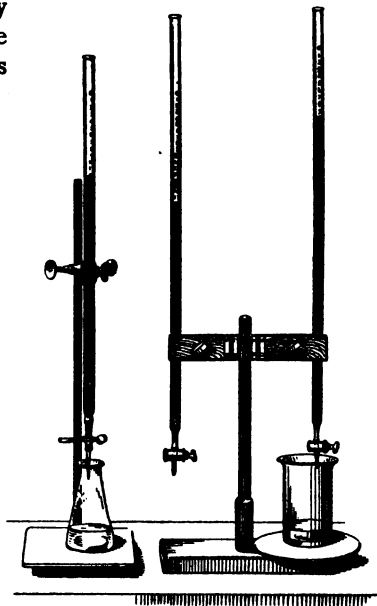

Fig. 11.

Fig. 12.

of a pinch-cock. Fig. 12 shows the two forms of apparatus. The burette is graduated almost throughout the length, the graduations being usually tenths of a cubic centimetre. The size most commonly used has a capacity of 50 c.c. For ordinary use the common retort-stand and clamp shown to the left in the figure make a very convenient stand for holding burettes. If desired, several can be supported upon the same retort-stand. The instrument is filled by means of a small funnel placed in the top (which should be removed afterwards, lest any adhering drops fall into the burette), until the liquid is considerably above the topmost graduation. The tap or pinch-cock is then momentarily opened, in order that the liquid may

sweep out before it the air which is contained in the tap and jet. This will not be successfully accomplished if the tap or pinch-cock is only *gradually* opened, as the liquid then slips down the walls of the narrowed portions and leaves air-bubbles in the tubes, which it is absolutely necessary to remove before the instrument can be used with exactness.

To read a burette.—Owing to the action of capillarity, the surface of a liquid contained in a glass tube is not *plane*, but *curved*.

This curved surface is called the *meniscus*. Fig. 13 shows the meniscus in the case of water contained in a burette.

In reading the burette, it is usual to take the graduation
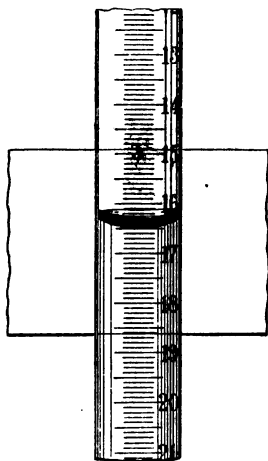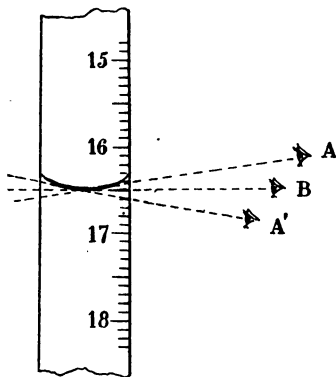
FIG. 13.   FIG. 14.

which coincides with the lowest point of the meniscus. Thus, in Fig. 14 the correct reading would be 16·5. If, as sometimes happens in certain lights, the line of the curve is not very clearly visible, it may usually be made quite distinct by holding behind the tube a piece of white paper, inclining it slightly upwards, as in Fig. 13. In order to make a correct reading, it is necessary that the eye of the observer should be in the same horizontal plane as the surface of the liquid. The reason for this will be evident from the diagram (Fig. 14), where an error of one graduation would arise by reading from either of the positions A or A' instead of from B.

A simple device to ensure that the readings of a burette shall be consistently made from a correct point of observation is shown in Fig. 15. It con-
sists merely of a narrow strip of card folded in the middle, with the two free ends pinned together with a paper-fastener. This is slipped over the burette, and while it allows of being easily slid up and down the tube, it will also hold itself in any position in which it may be put. When taking a reading, this little clip is placed so that its upper edge is just a little below the level of the liquid: then, when the eye is in such a position

FIG. 15.

that the back and front edges of the clip just coincide, it will also be practically in the same horizontal plane as the bottom of the meniscus.
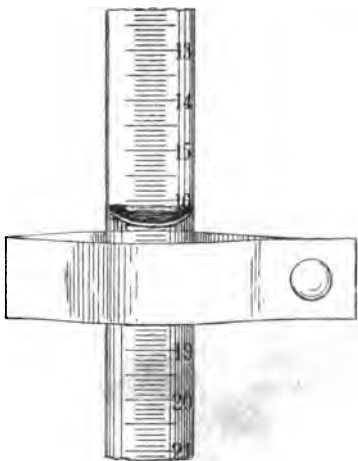
Indicators.—It is essential to a volumetric process that the exact point when the chemical action is complete should be readily discerned. This is often accomplished by the presence of some substance which will change its colour as soon as the reagent is in the slightest excess. Such substances are called indicators. The most familiar example is litmus, which is reddened by acid and rendered blue by alkalies. Sometimes the reagent itself is the indicator; potassium permanganate, for instance; so long as this reagent is being utilised in the chemical action of oxidation, so long will the violet colour of each added drop be destroyed, but the first drop after the completion of the reaction imparts its violet tint to the liquid. When acids or alkalies are being determined, either *litmus* or *methyl orange* will answer the purpose of an indicator. When carbon dioxide is eliminated in the neutralisation, as when alkali carbonates are being used, litmus cannot be used *unless the liquid be boiled*,

since otherwise the CO_2 dissolving in the liquid would exert an *acid* action on the litmus. Under these circumstances methyl orange is preferable.

Methyl orange gives an orange-coloured solution (yellow in presence of alkali) which is changed to a pink-red by acids. Only one or two drops of a *very dilute* solution should be used.

Most volumetric processes belong to one of the three following classes :—

1. *Those that are based upon the neutralisation of acids and alkalies.*

2. *Those based upon processes of oxidation or reduction.*

3. *Methods by precipitation.*

In the following section two or three typical examples of each of these classes will be given.

I. Volumetric Exercises based on Neutralisation of Acids and Alkalies.

The first requisite is a standard solution of some acid or alkali which can readily be prepared with a reasonable degree of accuracy, to serve as a foundation or basis upon which to make up any other acids or alkalies that may be required, for obviously we must *start* with a solution whose strength is exactly known before it can be used as a measure of the acidity or alkalinity of some other solution. To attempt to start with either sulphuric or hydrochloric acid would involve serious complications, for although we may exactly weigh out 49 grams of strong sulphuric acid in order to dilute it to the strength required for a normal solution, we do not know what is actually the strength of the strong sulphuric we are weighing. It certainly is *not* H_2SO_4 and nothing else, but is H_2SO_4 + an unknown amount of water.

Caustic soda, again, rapidly absorbs moisture from the air —how much of this it has already absorbed while in its bottle is an unknown quantity, and, moreover, it quickly absorbs more while it is actually being weighed out. Therefore, with however much care and expedition we weigh out 40 grams of caustic soda and make it up to a litre of solution, we are still ignorant of the *exact* weight of the alkali the solution contains. These difficulties are avoided by starting with sodium carbonate.

Normal Sodium Carbonate

(53 *grams of* Na_2CO_3 *per litre*)

In order to obtain this salt in a state of purity, it is prepared by heating the purest sodium bicarbonate to a dull red heat until no further loss of carbon dioxide and water takes place.[1] Theoretically, 84 grams of bicarbonate should yield 53 of the normal salt; a slight excess of this proportion, therefore, should be employed. To prepare half a litre of the standard solution, about 43 grams of the pure sodium bicarbonate are heated in a weighed platinum dish to a low red heat for about 10 or 15 minutes. The salt must not be allowed to fuse. It is then cooled in a desiccator and weighed. To ensure that the decomposition has been completed, the dish is again heated for another 10 minutes, and, after cooling in the desiccator, weighed again. The weight of the salt (after deducting the weight of the dish) will be a little over 26·5 grams. By means of a clean spatula or pen-knife, a small quantity is removed, so as to bring the weight to exactly 26·5 grams, the operation being performed without undue exposure of the dry salt. The contents of the dish are then washed out into a beaker, the dish being thoroughly rinsed with warm water, and the salt completely dissolved by stirring the mixture with a glass rod. The solution is then carefully poured into a half-litre flask, the beaker being several times rinsed with water. The flask is then carefully filled to the graduation mark, after which the stopper is inserted, and the contents thoroughly mixed by shaking.

Instead of bringing the weight of the sodium carbonate to the exact quantity required for half a litre of solution, the whole of the salt in the dish may be employed, and the exact volume of water which will be required in order to make the solution of normal strength is calculated. Thus, suppose the weight of sodium carbonate in the dish after heating is 26·749 grams, instead of 26·5 ; then—

$$26·5 : 26·749 :: 500 \text{ c.c.} : 504·7 \text{ c.c.}$$

[1] Of the so-called " pure " salts of commerce, the bicarbonate is of a higher degree of purity than the normal salt.

Hence, after the solution has been made up to the graduation mark in the manner described above, 4·7 c.c. of water are added from a burette, and the solution then finally shaken up to ensure thorough mixing.

This solution, if its preparation has been carefully carried out, should now be of exact "normal" strength, and, as all analytical determinations in this class are made on the basis of this assumption, it is evident that great care should be taken to ensure accuracy.

1 c.c. of this solution then contains 0·053 gram Na_2CO_3; it is therefore capable of neutralising, or is *equivalent to* 0·049 gram H_2SO_4, and 0·0365 gram HCl.

By means of this standard sodium carbonate, it is now easy to prepare either standard sulphuric or hydrochloric acid.

Normal Sulphuric Acid

(49 *grams of* H_2SO_4 *per litre*)

The specific gravity of ordinary oil of vitriol being about 1·8, 49 grams will be rather less than 30 c.c. Hence, if this volume be measured out and diluted up to a litre, a solution will be obtained which will have a rough approximation to the required strength. If this solution is then titrated with the standard sodium carbonate, its actual strength can be ascertained; and by calculation, the volume of water which must be added in order to bring it to the exact normal strength is determined.

Dilution of the Acid.—Thirty cubic centimetres of pure sulphuric acid are gradually poured into about 150 c.c. of water in an ordinary flask. The mixture is then cooled by holding the flask under the water-tap, and allowing a stream of water to run over it, at the same time shaking the liquid round within the vessel. When quite cold, the solution is transferred to a litre flask, and the volume made up to the 1000 c.c. mark by the addition of cold water.

Titration of the Acid.—A burette is first filled with the dilute acid,[1] care being taken to remove all air-bubbles from

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[1] Whenever burettes or pipettes are employed for measuring standard solutions, they must either be *dry* before use, or, if moist, they must be

the tap, as explained on p. 123. Twenty-five cubic centimetres of the normal sodium carbonate are then transferred by means of a pipette[1] to a small beaker, and a single drop of the methyl orange indicator is added. The beaker is then placed upon a white glazed tile beneath the burette, and the acid gradually run into the alkaline liquid, the solution being gently rotated in order to ensure thorough mixing after each addition of acid. At first 2 or 3 c.c. of the acid may be added at a time; but as the point of neutrality is approached, smaller and smaller quantities are added at once, until they are reduced to a few drops only, and at last the addition of a single drop produces a permanent pink colour in the liquid.

Correction of the Acid.—The exact volume of the acid which has been used in order to neutralise the 25 c.c. of normal sodium carbonate is noted, and from it the volume of water which must be added in order to make the acid exactly normal is calculated. Thus, suppose instead of 25 c.c. of acid, 23·8 c.c. were used in neutralising 25 c.c. of the normal alkali; then—

$$25 : 23\cdot8 :: 1000 : 952$$

That is to say, 952 c.c. of the acid contain as much sulphuric acid as should be contained in 1000 c.c., if it were exactly normal. If, therefore, 952 c.c. of this acid be measured out into a litre-flask, and the volume be then made up to the litre by the addition of water, a correct normal acid will be obtained.

The solution thus obtained should be once more titrated with the sodium carbonate.

When the strength of the acid is very nearly, but not *exactly*, normal, instead of attempting to bring it to the precise normal strength, it may be used as it is, and a correction introduced every time by means of a factor. For example, suppose every 25 c.c. of normal sodium carbonate required 24·6 c.c. of the acid instead of 25 c.c. in order to neutralise it; then—

$$24\cdot6 : 25 :: 1 : 1\cdot016$$

That is to say, every cubic centimetre of this acid is equal to

first rinsed out with a small quantity of the solution; otherwise that portion which is measured out for use would be slightly diluted by the water adhering to the walls of the instrument.

[1] See above note.

K

1·016 c.c. of an exactly normal acid; therefore, if the number of cubic centimetres of this acid used in any titration be multiplied by the factor 1·016, the result will be the number of cubic centimetres which would have been required if the acid had been strictly normal.

Or again, if the acid should be a little *weaker* than the exact normal, a similar correction can be made. Thus, suppose 25 c.c. of normal sodium carbonate required 25·2 c.c. of acid instead of 25 c.c. in order to reach the neutral point, then—

$$25\cdot2 : 25 :: 1 : 0\cdot992$$

That is to say, each cubic centimetre of the acid is in reality only equivalent to 0·992 c.c. of normal acid; therefore in this case 0·992 is the factor by which the number of cubic centimetres of this acid used would have to be multiplied in order to convert them into cubic centimetres of normal acid.

Titration of the Acid, using Litmus as Indicator.—In the absence of methyl orange, the titration of the acid by means of sodium carbonate may be carried out with litmus as the indicator. In this case, however, it is necessary to boil the solution in order to expel the carbon dioxide. The acid is added gradually, until the colour of the litmus changes from blue to purple-red. The solution is then boiled, and as the carbon dioxide is expelled the colour returns to the original blue shade. After boiling for a few minutes, acid is admitted in small quantities, and the liquid boiled up after each addition, until at last the addition of a single drop gives a permanent bright-red colour, which does not change on boiling.

Having now prepared and standardised the normal sulphuric acid, its exact strength or *value* should be plainly indicated on a label. Thus, in the case of the first of the two examples above, the factor 1·016 should be written on the label. It is also useful to indicate the actual value of the acid per cubic centimetre in terms of alkali, which is readily calculated. For example, 24·6 c.c. of the acid in question contains as much H_2SO_4 as would be contained in 25 c.c. were the solution *strictly* normal.

One litre of this slightly stronger acid, therefore, instead

of containing 49 grams H_2SO_4, would contain 49·8 grams, or
1 c.c. = 0·0498 gram H_2SO_4.

Then to find its value in terms of Na_2CO_3, we have the
proportion—

$$0·049 : 0·0498 :: 0·053 : 0·0538$$

Similarly for NaHO—

$$0·049 : 0·0498 :: 0·040 : 0·0406$$

The label for this acid should therefore carry these figures—

$$1 \text{ c.c.} = 0·0538 \text{ gram } Na_2CO_3$$
$$= 0·0406 \quad „ \quad NaHO$$
$$= 0·0315 \quad „ \quad Na_2O$$

Examples of Analyses by means of Standard Acids and Alkalies

1. **Determination of the Total Alkali** in a sample of
soda-ash—

From 5 to 10 grams of the soda-ash are weighed out into
a flask, and dissolved in cold water, and the solution made up
to 500 c.c. in a half-litre flask, and thoroughly shaken. Then,
by means of a pipette, 50 c.c. of this solution are transferred
to a small flask and a drop of methyl orange added. Standard
acid is run in from a burette (see note on p. 128) until the pink
colour is visible.[1]

At least *two* determinations should be made after the first
rough trial experiment, and if they fairly agree the mean may
be taken as the basis for calculating the result.

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[1] When neutralising a solution of an entirely unknown degree of
alkalinity, one must either add the reagent a few drops at a time from
the beginning—often a slow process, which may occupy much time—or, if
it is added in larger quantities one must run the risk of overstepping the
mark. In practice it is best to adopt the second plan for the first experi-
ment, so as to ascertain roughly the volume of acid required. Then a
second measure of 50 c.c. is taken, when the acid may be fairly quickly
run in until within 1 or 2 c.c. of the required volume, after which it should
be added drop by drop.

EXAMPLE.—Weight of soda-ash taken = 8·75 grams.
Dissolved and made up to 500 c.c.
(1) 50 c.c. taken, vol. of acid reqd. between 13 c.c. and 14 c.c. (rough).
(2) „ „ „ „ „ 13·2 c.c.
(3) „ „ „ „ „ 13·4 „
Mean = 13·3 „
Strength of standard acid, 1 c.c. = 0·0315 Na$_2$O

Therefore weight of Na$_2$O in 50 c.c. of the alkali solution $\left.\right\} = \left\{\begin{array}{l}13\cdot3 \times 0\cdot0315 = 0\cdot41895 \\ \text{gram}\end{array}\right.$

And since 50 c.c. = one-tenth the total, therefore the weight of Na$_2$O in the original weight of soda-ash $\left.\right\} = 4\cdot1895$ grams

Hence the percentage of Na$_2$O (or total alkali) $\left.\right\} = \dfrac{4\cdot1895 \times 100}{8\cdot75} = 47\cdot08$

A volumetric determination of an acid by means of standard sodium carbonate is carried out exactly as in the operation of standardising the normal acid solution, except that a measured volume of the acid of unknown strength is transferred by means of a pipette to a small flask, a drop of methyl orange added, and the standard alkali added from a burette until the pink colour of the indicator is just destroyed.

Other Standard Acids and Alkalies.—It will be obvious that the standard sodium carbonate and sulphuric acid can be used for preparing other standard acids and alkalies, such as caustic soda or hydrochloric acid. In the former case about 23 or 24 grams of the purest available caustic soda are dissolved in water and made up to 500 c.c. This gives a solution stronger than the normal, but whose strength is practically an unknown quantity. To ascertain its exact strength it is titrated with the standard acid, using 25 c.c. of the alkali measured with a pipette, and one drop of methyl orange as indicator. From this determination the volume of water necessary to add in order to dilute the alkali to the normal is calculated, as explained in the case of sulphuric acid.

II. Exercises based on Processes of Oxidation and Reduction.

Three oxidising agents will be considered, namely, potassium permanganate, potassium dichromate, and iodine.

A. *Decinormal Potassium Permanganate* (3·16 grams of KMnO₄ per litre).

To prepare this solution 3·2 grams (as near as possible) of the ordinary "pure" salt are weighed out and dissolved in water in a litre flask. When entirely dissolved the flask is filled to the graduation mark, and the contents well shaken.

Titration of Potassium Permanganate by means of Ferrous Sulphate. — An *exactly* deci-normal permanganate solution will contain 0·0008 gram available oxygen per 1 c.c. Therefore 1 c.c. is capable of oxidising 0·0056 gram of ferrous iron to the ferric state; it is then equivalent to this weight of iron. The aim of this titration is to determine with the greatest possible care the *exact* strength of the permanganate.   For this reason the ferrous sulphate is prepared by dissolving 0·5 gram of the purest soft iron wire in sulphuric acid, with exclusion of air, the wire being clean and free from rust.[1]

About 80 c.c. of dilute sulphuric acid (1 part acid to 5 parts water) are placed in a 250-c.c. flask fitted with a rubber cork and bent glass tube. The air in the flask is then expelled by removing the cork and introducing two or three crystals of pure sodium carbonate, the flask being in a vertical position. As soon as the carbonate has dissolved, the weighed quantity of iron is dropped in. The cork is then inserted, and the flask supported in the manner shown in Fig. 16, with the tube dipping into a solution of sodium carbonate in a small
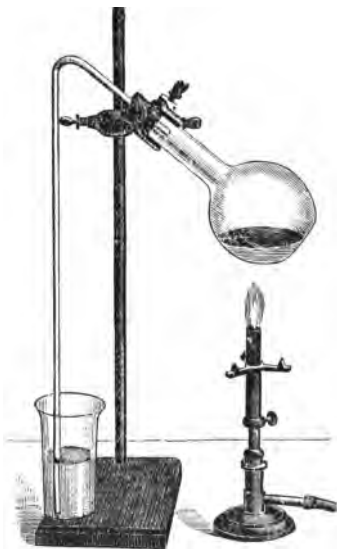
Fig. 16.

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[1] The fine iron binding wire used for flowers is the best for the purpose; it contains 99·6 per cent of iron.

beaker. The flask being in this inclined position, the fine spray thrown up during the solution of the iron strikes against the sides of the flask and falls back into the liquid. The flask is gently heated by means of a small flame until the iron is wholly dissolved, and only a few minute particles of carbon remain. The lamp is then withdrawn, and the flask allowed to cool. As it does so, the solution in the beaker is gradually drawn up the tube, but the first drops which enter the flask at once cause an effervescence of carbon dioxide which drives the liquid down again, and at the same time fills the flask with carbon dioxide. When it has partially cooled in this way, the cork is removed, and air-free distilled water (prepared by boiling the water, and again quickly cooling it) is added until the solution is within about 20 or 30 c.c. of the graduation mark. The flask is then closed with a rubber stopper, and the contents made quite cold by holding the vessel in a stream of cold water. The solution is then made up to 250 c.c. by the further addition of cold air-free water.

Fifty cubic centimetres of this solution are transferred by means of a pipette to a small flask, and diluted by the addition of about half the volume of air-free distilled water. The flask is placed upon a white tile, and the deci-normal permanganate solution added from a burette [1] until the colour of the reagent ceases to be destroyed, and a faint pink tint is imparted to the solution.

Four separate experiments should be made, taking 50 c.c. of the iron solution each time, in order to gain practice in judging when the first appearance of the permanent pink colour takes place. After the experience thus gained, in subsequent duplicate titrations the volume of the reagent used should agree to 0·1 of a cubic centimetre. From the results obtained, the exact strength of the permanganate is calculated ; thus—

0·5 gram of iron wire was dissolved in 250 c.c. of liquid. Fifty cubic centimetres of the solution therefore contain 0·1

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[1] For permanganate solutions a burette with a glass tap must be used, as this liquid acts upon rubber, thereby, of course, becoming altered in strength.

gram of iron.   But since the iron wire contained 99·6 per cent. of Fe, the actual weight of iron present in 50 c.c. of the solution was not 0·1 gram, but 0·0996 gram.

The mean of four titrations gave 17·69 c.c. as the volume of permanganate required.

Then 17·69 c.c. : 1 c.c. :: 0·0996 gram : 0·00563 gram

Therefore the solution is very slightly stronger than the exact deci-normal, since 1 c.c. should be equivalent to 0·00560 gram of iron ; it should therefore carry on its label its equivalent value, thus—

$$1 \text{ c.c.} = 0·00563 \text{ Fe}$$

Estimation of Iron in a Ferrous Salt.—As an exercise in the use of standard permanganate, an estimation of iron may be made in a ferrous salt, the exact composition of which is not known to the student.   It might be ferrous sulphate, or one of the double sulphates of ferrous iron and the alkalies. Three or four grams of the salt are weighed out, dissolved in water, and made up to 250 c.c. ; 50 c.c. of this are then transferred to a small flask, and 10 to 15 c.c. of dilute sulphuric acid added.   This is then titrated with the deci-normal permanganate. Suppose the following data obtained :—

Weight of salt taken = 3·5 grams

Dissolved and made up to 250 c.c.; 50 c.c. employed for each experiment.

Deci-normal permanganate used (mean of four experiments) = 17·8 c.c.

Value of permanganate, 1 c.c. = 0·00563 Fe

Therefore weight of Fe in 50 c.c. = 0·00563 × 17·8 = 0·1002 gram

Hence weight of iron in 3·5 grams of salt (*i.e.* in 250 c.c. of the solution) = 0·1002 × 5 = 0·501 gram

Therefore percentage of iron in compound $= \dfrac{0·501 \times 100}{3·5} = \mathbf{14·29}$

B. *Deci-normal Potassium Dichromate* (4·913 grams per litre)

4·913 grams of the pure, dry, powdered salt are exactly weighed out, dissolved in water in a litre flask, and the volume made up to the graduation mark. Being deci-normal, one litre will contain one-tenth of an equivalent of available oxygen, *i.e.* o·8 gram ; hence 1 c.c. = o·0008 gram available oxygen, and is equivalent to o·0056 gram Fe.

This solution may be used in a burette with a rubber tube and pinchcock.

Titration of Potassium Dichromate by means of Ferrous Sulphate.—The ferrous sulphate is prepared by dissolving pure iron in dilute sulphuric acid, with exclusion of air, precisely as described for permanganate, p. 133. An aliquot part of the solution—say 50 c.c.—is withdrawn by means of a pipette, and transferred to a small flask, and the dichromate solution gradually added from a burette.

In this process the end of the reaction is ascertained by means of a freshly made and dilute solution of potassium ferricyanide, used as an *outside* indicator. A number of drops of the ferricyanide are placed about upon a white plate or tile, and from time to time, during the addition of the dichromate, a drop of the mixture is withdrawn upon a glass rod and brought into contact with one of the drops of the indicator. At first a strong blue coloration is produced, but as the amount of ferrous salt is gradually diminished by the addition of the dichromate, the blue becomes less and less intense, until at last a drop of the liquid so tested fails to give any coloration. At this point the whole of the ferrous salt has been oxidised, and the reaction is therefore complete.[1]

The mean of two or three titrations is taken, and from it the exact strength of the dichromate calculated, as in the case of permanganate, and the true value of the solution in terms of iron is indicated on the label, *e.g.* 1 c.c. = o·00559 Fe, which would mean that the solution was just a little below the true normal strength.

In a number of instances, potassium dichromate may be

[1] It will be evident that it is absolutely essential to the success of this operation that the ferricyanide should be perfectly free from ferrocyanide, otherwise the oxidised iron will itself give rise to a blue coloration.

substituted for permanganate in volumetric analysis. This is the case, for example, with all estimations that are based upon the oxidation of ferrous to ferric salts.

Estimation of Iron in Iron Ores.—About 2 grams of finely powdered and dry red hæmatite are weighed out into a flask and boiled with a small quantity of strong hydrochloric acid, diluted with about half its own volume of water, until the whole of the iron has been extracted, and the residue is free from dark-coloured particles.

The next step consists in reducing the iron, which is at present either partially or wholly in the ferric state. This may be done by first diluting the liquid somewhat and introducing into it a few fragments of pure zinc (*i.e.* free from iron). A cork with a leading tube is then inserted. Hydrogen is evolved by the solution of the zinc in the acid liquid, and the iron existing in the *ferric* state is thereby reduced to the *ferrous* condition. The action is allowed to continue *until the zinc is entirely dissolved,* the process being aided towards the end by the application of heat. In order to test whether the reduction of the iron is complete, a drop of the liquid is withdrawn upon the end of a fine glass rod, and brought into contact with a drop of a solution of ammonium thiocyanate upon a white tile. Any remaining ferric salt will be revealed by the formation of the red colour; in which case the process must be continued by the addition of more zinc, and, if necessary, of more acid also. When the reduction is complete, the liquid is quickly cooled, and made up to 250 c.c.; 25 c.c. of this solution are then withdrawn with a pipette, transferred to a small flask, and titrated with the deci-normal dichromate. The presence of the zinc salt in the liquid interferes somewhat with the delicacy of the indicator,[1] so that several titrations should be made in order to practise the use of the indicator under these conditions.

Made in this way, the result of the analysis is the estimation

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[1] For this reason the reduction is often brought about by the use of stannous chloride, or by adding an alkali sulphite when iron is to be determined by dichromate. The presence of zinc salts is immaterial when ferrous permanganate is employed for the titration.

of the *total* iron in the ore. Very often iron ores contain a portion of the iron in the ferrous, and the remainder in the ferric, state. These may be separately determined by first dissolving a weighed quantity of the ore with exclusion of air, in the arrangement shown on p. 133. In this solution the ferrous iron is determined. Then a second weighed quantity is dissolved and subjected to the reducing agent as above described, and in this the *total* iron is estimated. The difference between these gives the ferric iron originally present.

This analysis can be carried out equally well with permanganate, but in this case an unnecessary excess of hydrochloric acid must be avoided, and the liquid well diluted before titration, for the reason that permanganate reacts upon hydrochloric acid with evolution of chlorine unless the acid is quite weak.

C. *Deci-normal Iodine Solution* (12·7 grams of iodine per litre).

The solution is prepared by weighing out as exactly as possible 12·7 grams of pure iodine, and adding to it in a litre flask a solution of 20 grams of potassium iodide in 200 c.c. of water. As soon as the iodine is entirely dissolved, the liquid is diluted up to 1 litre. If *strictly* deci-normal, 1 c.c. would contain 0·0127 gram iodine, and would be equivalent to 0·00355 gram chlorine and 0·0008 gram oxygen.

In presence of water and certain oxidisable substances (*i.e.* reducing agents), iodine unites with the hydrogen of the water, and the oxygen so eliminated oxidises the reducing agent. Thus arsen*ites* are converted into arsen*ates*, and thiosulphates into tetrathionates. As a deci-normal solution of sodium thiosulphate is required for many of the processes in which iodine is used, this may be used in order to standardise the iodine solution prepared as above.

Deci-normal Sodium Thiosulphate (24·8 grams of $Na_2S_2O_3,5H_2O$ per litre).

24·8 grams of the purest salt are weighed out into a litre flask, and dissolved in a moderate quantity of water. When wholly dissolved, the volume is made up to the graduation mark. If strictly normal, 1 c.c. will be completely oxidised by 1 c.c. of the deci-normal iodine solution.

Titration of Deci-normal Iodine with Sodium Thiosulphate. — Twenty-five cubic centimetres of the thiosulphate solution are transferred by means of a pipette to a small beaker, diluted with a little water, and two or three drops of clear starch solution added, to serve as an indicator. The iodine is then run in from a stoppered burette until a single drop gives a permanent blue colour.

This titration can equally well be performed in the reverse order, and as in many analyses with standard iodine the solutions are so used, the operation should here be practised in both ways. Transfer 25 c.c. of the iodine solution to a small beaker, and, *before adding the starch indicator*, run in the thiosulphate solution from a burette until the brown colour of the iodine has become paled to straw colour, then add the indicator, which, of course, produces a blue coloration. The thiosulphate is now added drop by drop until the colour is just discharged. The result obtained must be the same whichever way the operation is conducted.

If both solutions are exactly deci-normal,[1] 1 c.c. of iodine = 1 c.c. thiosulphate. If there is only a slight discrepancy, then the factor (see p. 129) should be indicated upon the label of each solution; for example, suppose 25 c.c. of the iodine required 24·9 c.c. thiosulphate, then 1 c.c. of the latter equals $25 \div 24·9 = 1·004$ c.c. iodine, and 1 c.c. of the iodine = 0·996 c.c. thiosulphate. On the other hand, should the titration show a wide disparagement between the two solutions, then one of them (the iodine) must be tested by another method (arsenious oxide).

Titration of Deci-normal Iodine with Arsenious Oxide. — The weight relation is expressed by the equation—

$$As_2O_3 + 2I_2 + 2H_2O = 4HI + As_2O_5$$

That is to say, 127 parts of iodine will oxidise 49·5 parts of arsenious oxide.

[1] It is, of course, *possible*, although very improbable, that the two solutions might be of exactly equivalent strength, although not exactly deci-normal ; that is to say, an error to exactly the same extent might have been made in preparing each.

4·95 grams of resublimed arsenious oxide are weighed out into a litre flask, and about 500 c.c. of water added. Then 30 grams of pure sodium bicarbonate are added, and the mixture slightly warmed and continually shaken, until the oxide is completely dissolved. The liquid is then cooled and diluted up to 1 litre : 1 c.c. of this deci-normal solution should be exactly equivalent to 1 c.c. of the iodine solution ; 25 c.c. are transferred to a small beaker, a few drops of the starch added, and the iodine solution run in until the blue coloration is permanent. From the result the exact strength of the iodine is calculated.

The estimation of arsenic in an unknown solution of an arsenious compound, or in an arsenite, is carried out by means of deci-normal iodine solution exactly as this titration.

Estimation of Sulphur Dioxide or a Sulphite.—As an illustration of the use of standard iodine and thiosulphate in conjunction, the following exercise may be carried out.

A dilute solution of sodium sulphite of unknown strength is taken, and 50 c.c. of it are transferred to a small beaker by means of a pipette. A measured volume of deci-normal iodine is added, well in excess of what is required to oxidise the sulphite, which is seen by the mixture having a brown colour. The excess of iodine present is then ascertained by titration with deci-normal thiosulphate added from a burette, the starch, as before, being added when the brown colour changes to yellowish. The excess of iodine thus determined, deducted from the total originally taken, gives the iodine which has been used to oxidise the sulphite, according to the equation—

$$Na_2SO_3 + I_2 + H_2O = 2HI + Na_2SO_4$$

That is to say, 127 parts of iodine are capable of oxidising 32 parts of SO_2 into SO_3 ; 1 c.c. of the iodine solution, therefore, is equivalent to 0·0032 gram SO_2.

Thus, suppose 50 c.c. deci-normal iodine to have been originally used, and that the titration required 15 c.c. of the thiosulphate, then $50 - 15 = 35$ c.c. of iodine solution were used in oxidising the SO_2 present in 50 c.c. of the unknown solution.

Then, since 1 c.c. iodine = 0·0032 gram SO_2—

0·0032 × 35 = 0·112 gram SO_2 in 50 c.c., *i.e.* 2·24 grams per litre

Estimation of Chlorine.—The element chlorine decomposes potassium iodide, liberating its equivalent of iodine; *i.e.* 127 parts of iodine are liberated by 35·5 parts of chlorine. If the iodine thus liberated is estimated by titration with a standard solution of sodium thiosulphate, indirectly the weight of chlorine which caused its liberation will be determined. In this way the strength of a solution of chlorine water could be determined; or the amount of *available chlorine* in bleaching powder (*i.e.* the chlorine which is evolved when the compound is acted upon by a dilute acid).

Estimation of Available Oxygen.—Many substances containing oxygen (*e.g.* certain peroxides, chromates, permanganates), when heated with hydrochloric acid, oxidise the acid with the evolution of an amount of chlorine equivalent to the oxygen so used. Thus MnO_2 contains *one* atom of available oxygen; and by the action of hydrochloric acid upon this oxide, this one atom causes the evolution of 2 atoms of chlorine; or 8 parts of O result in the evolution of 35·5 parts of Cl. If this chlorine is made to act upon potassium iodide, it in its turn liberates an equivalent of iodine, which can be estimated by means of the standard thiosulphate. The iodine is therefore the indirect measure of the oxygen, and from this obviously the amount of the oxygen compound can be calculated.[1]

III. Processes based on Precipitation.

Deci-normal Silver Nitrate (17·00 grams per litre).—To prepare a quarter-litre, 4·25 grams of pure silver nitrate are weighed out into a 250-c.c. flask and dissolved in water, and the solution diluted up to the graduation mark; 1 c.c. of this solution, if strictly deci-normal, will contain 0·0108 gram Ag, and is equivalent to 0·00355 gram of Cl.

[1] For details of such processes as are here merely hinted, the student must consult larger manuals of analysis.

Estimation of Chlorine in a Soluble Chloride.—As an exercise upon this process, a dilute solution of common salt of unknown strength may be analysed.

Twenty-five cubic centimetres of the solution are transferred to a small beaker by means of a pipette, and three or four drops of a solution of potassium chromate (the normal salt) are added. The deci-normal silver solution is then gradually run in until a permanent reddish tinge is visible. The red colour is due to the formation of silver chromate, which does not begin to form until the whole of the chloride present has been precipitated as silver chloride. The titration should be repeated once or twice to gain practice in the use of this indicator.

Estimation of Silver.—This process is exactly the reverse of the former, and is carried out by means of a deci-normal solution of sodium chloride. This solution is prepared by dissolving 5·85 grams of pure sodium chloride in water, and diluting the solution up to 1 litre. In conducting the titration the indicator must not be added to the silver solution to be estimated, but to the sodium chloride. A measured volume, 25 c.c., of the latter is transferred to a beaker, coloured with the indicator, and the silver solution delivered from a burette. One cubic centimetre deci-normal NaCl contains 0·00355 gram Cl, and is therefore equivalent to 0·0108 gram Ag.

Deci-normal Ammonium Thiocyanate (7·6 grams $(NH_4)CNS$ per litre).—When ammonium thiocyanate is added to silver nitrate, a white precipitate of AgCNS is formed; and if a drop of a solution of a ferric salt (not the chloride) be added to the silver solution, the development of the familiar blood-red colour will indicate the completion of the precipitation.

About 8 grams of the thiocyanate are weighed out and dissolved to make 1 litre of solution; 25 c.c. of deci-normal silver nitrate are transferred to a small flask, and 3 or 4 c.c. of ferric sulphate solution added (previously made by dissolving a crystal of ferrous sulphate in a little water in a test-tube, adding about half its volume of strong nitric acid and boiling for a few minutes, then diluting with about twice the volume of water). The ammonium thiocyanate is then run in from a burette. As each drop enters, a red colour momentarily appears, but

disappears on gently shaking the flask. The precipitation is complete when a single drop causes a permanent red tint. From the volume used the real strength of the thiocyanate is ascertained, and the amount of dilution it requires to bring it to exact deci-normal strength is calculated ; 1 c.c. deci-normal thiocyanate should be equivalent to 0·0108 gram Ag, or 0·00355 gram Cl.

Estimation of Silver in a Silver Alloy.—A weighed piece of the alloy (such as a small silver coin) is dissolved in nitric acid, and the solution made up to 250 c.c. ; 25 c.c. of this are transferred to a small flask, the ferric sulphate indicator added, and the deci-normal thiocyanate run in from a burette until the red coloration is obtained. From this titration the percentage of silver in the alloy is calculated.

ABRIDGED TABLE OF ATOMIC WEIGHTS (APPROXIMATE VALUES)

Aluminium	... ...	Al	... 27
Antimony	... ...	Sb	... 120
Arsenic	... ...	As	... 75
Barium	... ...	Ba	... 137
Bismuth	... ...	Bi	... 208
Boron	... ...	B	... 11
Bromine	... ...	Br	... 80
Cadmium	... ...	Cd	... 112
Calcium	... ...	Ca	... 40
Carbon	... ...	C	... 12
Chlorine	... ...	Cl	... 35·5
Chromium	... ...	Cr	... 52
Cobalt	... ...	Co	... 59
Copper (*cuprum*)	... ...	Cu	... 63·5
Fluorine	... ...	F	... 19
Hydrogen	... ...	H	... 1
Iodine	... ...	I	... 127
Iron (*ferrum*)	... ...	Fe	... 56
Lead (*plumbum*)	... ...	Pb	... 207
Lithium	... ...	Li	... 7
Magnesium	... ...	Mg	... 24
Manganese	... ...	Mn	... 55
Mercury (*hydrargyrum*)	... ...	Hg	... 200
Nickel	... ...	Ni	... 59
Nitrogen	... ...	N	... 14
Oxygen	... ...	O	... 16
Phosphorus	... ...	P	... 31
Potassium (*kalium*)	... ...	K	... 39
Silicon	... ...	Si	... 28
Silver	... ...	Ag	... 108
Sodium	... ...	Na	... 23
Strontium	... ...	Sr	... 87·6
Sulphur	... ...	S	... 32
Tin	... ...	Sn	... 119
Zinc	... ...	Zn	... 65·4

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THE END